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LOWER OXIDATION STATES IN GALLIUM HALIDES

by

Richard K. McMullan

A Dissertation Submitted to the
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In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1956

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I. INTRODUCTION

Although the chemistry of tripositive gallium has been extensively studied, knowledge of the lower oxidation states, particularly in the halide systems, is quite limited (1,2). Only the chalkogenides (i.e., the oxide, sulfide and selenide) of gallium(I) have been reported, while among the halides the existence of only gallium dichloride has been substantiated.

In the gallium subgroup, the distribution of the valence electrons as ns^2np^1 suggests the possibility of both the + 3 and + 1 oxidation states, corresponding respectively to the involvement of all the electrons and of only the single p electron in bonding. The existence of the + 1 oxidation state would result from the presence of an "inert pair" of s electrons in the outermost electronic level of these atoms. This concept of non-bonding ns^2 electrons, as proposed by Sidgwick (3), has been frequently used to correlate observed lower oxidation states with the valence electron configuration of the representative group elements. However, the existence of gallium dichloride cannot be explained on this basis since divalent gallium would involve a single non-bonding electron.

In the gallium group, the stability of the + 1 oxidation state increases with increasing atomic weight of the elements, the same trend that is observed among the other representative

groups. Only for thallium are the unipositive compounds stable toward disproportionation both in aqueous solution and in the solid state. A few unipositive indium compounds, the halides and chalkogenides, are known in the solid state, but in water these disproportionate into indium(III) and metal (4,5).

Although the gallium(I) halides have not been obtained as solid compounds, their presence in the gas phase has been detected spectroscopically at high temperatures (6,7). Calculations based on the estimated thermodynamic values of Brewer et al. (8) indicate that these compounds should be unstable with respect to disproportionation in the solid state. Nevertheless, the presence of unipositive gallium as a solute species in fused gallium dichloride has been suggested to account for the slight solubility of gallium in that system. The monochloride could not be isolated, however, since the solution separated into the original components upon solidification (9). Further evidence for the existence of unipositive gallium in solution has been obtained from the anodic oxidation of gallium in either glacial acetic acid or liquid ammonia (10,11).

As previously noted, the chalkogenides are the only gallium(I) compounds reported to exist in the solid state. Gastinger (12) reported the preparation of Ga_2O, although he

gave no quantitative experimental details to substantiate the work. Brukl and Ortner (13) obtained Ga_2S as a sublimate after reducing Ga_2S_3 with hydrogen at 400°. Klemm and Vogel (14) observed Ga_2Se in the thermal analysis of the gallium-selenium system.

The gallium dihalides (chloride, bromide and iodide) were first prepared by de Boisbaudran in 1881 by the reduction of the trihalides with gallium at approximately 200° (15). Since that time, only the dichloride has received any significant attention, and Einecke (16) has even expressed doubt as to whether the diiodide was ever isolated. According to Laubengayer and Schirmer (17), gallium dichloride is a white, crystalline solid which melts at 170.5° to give a colorless, strongly-refracting liquid. The boiling point reported by de Boisbaudran is 535°, but Laubengayer and Schirmer found that above 200° disproportionation into the metal and trichloride becomes appreciable. In the presence of water vapor, gallium dichloride deliquesces to produce a brown, amorphous solid. In water a similar material is formed which slowly reduces the water with the evolution of hydrogen. Gallium dichloride dissolves in benzene apparently without reaction to the extent of 4.5 g. per 100 g. of solvent (9).

The contention that the dihalides represent true divalency of gallium appears to be questionable. Magnetic susceptibility measurements by Klemm and Tilk (18) demonstrated that the dichloride is diamagnetic in the solid state, whereas gallium(II) should show a paramagnetism corresponding to the spin of one unpaired electron. As a result of this evidence, they suggested that the odd electrons of two $GaCl_2$ units were paired in metal-metal bond formation, presumably as $Cl_2Ga\text{-}GaCl_2$.

Laubengayer and Schirmer (17) attempted to measure the vapor pressure and vapor density of gallium dichloride*, but due to extensive disproportionation the results were somewhat ambiguous. In the vapor pressure region, the system was found to be divariant, a fact which was not explained. The apparent molecular weights calculated from the vapor density data decreased with increasing temperature and approached that of $GaCl_2$. The authors interpreted these results qualitatively in terms of the gaseous species $GaCl_2$, Ga_2Cl_4, $GaCl_3$ and Ga_2Cl_6, which may be related by the equilibria

$$Ga_2Cl_4 = 2GaCl_2 \qquad (1)$$

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*As a matter of convenience, these compounds will be referred to as gallium dihalides without implication as to the oxidation state of gallium or the formula weight of the compounds.

$$3Ga_2Cl_4 = 4GaCl_3 + 2Ga_{(l)} \qquad (2)$$

$$Ga_2Cl_6^{*} = 2GaCl_3 \qquad (3)$$

Thus, they presented these data as evidence that the vapor contained some $GaCl_2$ molecules in which gallium showed the anomalous valence of two. Further, the implication was made that the dimeric species Ga_2Cl_4 contained the gallium-gallium bond postulated by Klemm and Tilk.

The structure $Ga(I)[Ga(III)Cl_4]$ has also been proposed to account for the diamagnetic properties of gallium dichloride (20). However, this formulation has been deemed somewhat unsatisfactory since gallium(I) chloride has not been isolated. Compounds of the formula type $M(I)[Ga(III)Cl_4]$, where M(I) is an ammonium or alkali metal ion, have been prepared and examined by Friedman and Taube (21). Although no structural data are available, it may be presumed that discrete $GaCl_4^-$ ions exist in the crystals of these compounds. If gallium dichloride is $Ga(GaCl_4)$, the vapor density measurements of Laubengayer and Schirmer can be explained without

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*Vapor density measurements (17) show that gallium trichloride exists largely in the vapor state as the dimeric species. Electron diffraction studies (19) indicate that in this unit each gallium atom is surrounded tetrahedrally by four chlorine atoms, with two of the six chlorine atoms acting as bridging groups.

postulating $GaCl_2$ molecules, since an equal molar mixture of GaCl and $GaCl_3$ would have the same vapor density as $GaCl_2$.

The dihalide series of compounds have also been reported for indium (22,23) and thallium (24,25). Klemm and Tilk (18) found that solid $InCl_2$ is diamagnetic; accordingly, the compound has also been formulated as either $Cl_2In\text{-}InCl_2$ (18) or $In(I)[In(III)Cl_4]$ (20). The latter structure is perhaps more acceptable for these compounds than for the compounds of the corresponding gallium series, since indium(I) and thallium(I) halides have been isolated. However, there is little experimental evidence to support either structure. From the X-ray powder diffraction data of $InCl_2$ and $SnCl_2$, Aiken et al. (26) suggested that the indium salt has the ionic structure $In^+ InCl_4^-$, isomorphous with $Sn^{+2} SnCl_4^{-2}$. However, the powder data do not clearly indicate isomorphism and, moreover, $SnCl_2$ has not been shown to have the structure proposed. On the other hand, the existence of the ions In^{+2} and In_2^{+4} as well as In^+ has been postulated to account for the reducing equivalents observed when aqueous solutions of In^{+3} are equilibrated with metallic indium (27). In the case of the thallium salts, the phase diagram of the TlCl-$TlCl_3$ system would show the intermediates $TlCl_2$ and Tl_2Cl_3 (25). These can be formulated as $Tl(TlCl_4)$ and $Tl_3(TlCl_6)$,

respectively, although supporting structural evidence has not been reported.

In summary, the preceding discussion points out that the gallium(I) halides have never been observed in a condensed state and, further, that the gallium dihalides, although known to exist, have never been studied sufficiently to allow an elucidation of the structural unit. Therefore, the primary objectives of this research were:

1. To ascertain whether the gallium(I) halides exist in a condensed state and whether they can be isolated as pure solids.
2. To determine the basic structural unit in the gallium dihalides and thereby establish the oxidation state or states present in these compounds.

II. MATERIALS

The compounds studied in this work were sensitive to moisture and oxygen and consequently were prepared and handled in a vacuum system. Transfers of gallium halides to powder pattern tubes, weighing capsules, etc. were carried out in a dry box through which circulated helium that had been dried with phosphorus pentoxide.

A. Gallium(III) Chloride

In the procedure described below, gallium trichloride of high purity was prepared by the direct union of gallium (99.95%, Aluminum Company of America) and chlorine (Matheson C. P.), followed by sublimation *in vacuo*.

The apparatus used in the preparation consisted of a segmented glass train, which had a gas inlet tube sealed to one end and a stopcock and ball-joint sealed to the other. Three fragile ampules were sealed on the segment nearest the stopcock. The apparatus was flamed out under vacuum, filled with dry helium, and supported in a horizontal position. Chlorine diluted with helium was passed through concentrated sulfuric acid, then over the gallium contained in the segment adjacent to the inlet tube, and the unreacted gases subsequently

discharged into a sodium sulfite solution. After the metal was completely oxidized, the system was flushed with helium and sealed from the gas source. The train was thoroughly evacuated and the product triply sublimed. The portion containing the salt was sealed from the vacuum line, the trichloride sublimed into the attached ampules, and these detached from the system.

B. Halogens

Bromine (Eimer and Amend Reagent Grade) and iodine (Baker's Reagent Grade) were purified in a glass train similar to that used in the gallium trichloride preparation. The halogens were first sublimed or distilled from phosphorus pentoxide, then after two additional transfers, condensed into fragile ampules for storage.

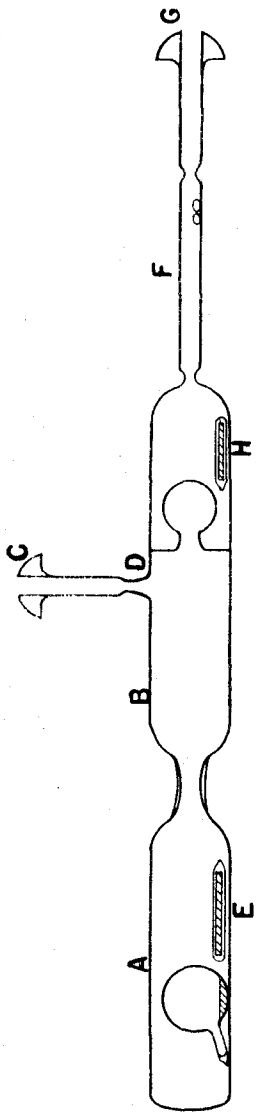
C. Gallium Dihalides

Two reactions for the preparation of the gallium dihalides have been used in this research. These were: (a) the reduction of the gallium trihalides with gallium (used for $GaCl_2$), and (b) the direct union of gallium and the halogen (used for $GaBr_2$ and GaI_2).

In the three preparations, stoichiometric quantities of the reactants were combined in the apparatus shown in Figure 1. A weighed ampule of either bromine, iodine or gallium trichloride purified according to the method described in A and B was placed with glass-encased bar magnet E in tube A, and the end of the tube sealed. The apparatus was thoroughly evacuated through ball-joint C and then sealed at the constriction D. The ampule was punctured by the magnet, and the contents of the ampule condensed in tube B. After a quantitative transfer, tube A was sealed from tube B, opened, and the broken ampule reweighed to determine the weight of the material transferred. The calculated weight of gallium was placed in section F, and that section evacuated through ball-joint G and sealed from the vacuum system. The barrier between B and F was broken with magnet G, the contents of B condensed in F, and the reactants contained in F sealed from the system.

In the gallium dichloride preparation the reactants were maintained in the fused state at 180° until the metal was completely consumed. In the direct union of bromine or iodine with gallium, the initial reaction was carefully controlled by cooling with an air blast or a dry ice pack until the halogen was consumed in the formation of the gallium trihalide. The subsequent reduction of the trihalide was

Figure 1. Apparatus for the Preparation of Gallium Dihalides


G
F
H
C
D
B
A
E

effected at temperatures a few degrees above the melting points of the products.

The preparations described above have been found to be the most convenient and satisfactory methods for obtaining pure gallium dihalides. Before these techniques were developed, methods similar to those described by earlier investigators (15,17) were employed. These methods required fractional sublimation of gallium trihalide from a dihalide-trihalide mixture prepared by incomplete halogenation of gallium or by the incomplete reduction of gallium trihalide by gallium. In this purification, removal of the excess trihalide was an inexact operation since disproportionation occurred at the temperatures necessary to remove the trihalide at an appreciable rate.

An interesting problem was encountered in the preparation of gallium triiodide by the reaction of gallium with excess iodine. Apparently, iodine was tightly bound to the salt, for a sample had the composition $GaI_{3.64}$ after three high-vacuum sublimations. Since the iodine-complex mixture could not be used for the preparation of gallium diiodide by the quantitative procedure described, the alternate method for direct preparation from the elements was developed.

D. Gallium (I) Tetrachloroaluminate

Synthesis of this compound was effected by the reduction of gallium trichloride with metallic aluminum (A. D. McKay 99.99%) according to the reaction

$$4GaCl_3 + 3Al = 3Ga(AlCl_4) + Ga . \qquad (4)$$

By a procedure similar to that used in the preparation of the gallium dihalides, 1.6122 g. (9.156 millimole) of gallium trichloride was combined with 0.1850 g. (6.859 millimole) of aluminum, and the mixture maintained at 190° in the fused state for three days. The metal phase produced was separated from the salt and identified as gallium by its melting point. The mole ratios $GaCl_3/Ga$ = 4.009 and Al/Ga = 3.003 calculated from the weights of the materials used and the weight of gallium produced indicated that the above reaction was complete.

E. Silver Tetrachlorogallate (III)

In order to prepare this compound, 1.1660 g. (6.622 millimole) of gallium trichloride and 0.9494 g. (6.623 millimole) of silver chloride were combined *in vacuo* by the method

previously described and the mixture fused at 170°. The silver chloride (Fisher Scientific Co. C. P.) was vacuum dried before use.

F. Benzene

'Baker Analyzed' Reagent grade benzene (thiophene free) was distilled in a thirty-plate Oldershaw column at a 30-1 reflux ratio. The fraction retained boiled at 80.12 ± 0.03° (corrected to 760 mm pressure). The distillate was redistilled *in vacuo* from calcium hydride and then stored over calcium hydride for later use.

G. Chlorobenzene

Eastman Kodak white label chlorobenzene was distilled in the Oldershaw column at a 30-1 reflux ratio. A constant boiling middle portion, one-fourth of the total amount used, was retained for use. The boiling point (corrected to 760 mm.) was 132.08°.

III. APPARATUS AND EXPERIMENTAL PROCEDURES

A. Phase Diagram of the System Gallium-Gallium Triiodide

The apparatus used for the determination of the melting points consisted of a 2.5 in. by 8 in. cylindrical aluminum block, through which a 6 mm. sample hole had been drilled longitudinally. The block was centered in a horizontal 2 5/8 in. i.d. by 12 in. cylindrical furnace. A slit for viewing the sample in the cylinder was cut through the furnace and block near the center, and a light source positioned behind it. The furnace temperature was controlled by a Powerstat and a Celectray controller. Since the heat capacity of the block was quite large, there was essentially no temperature gradient along the sample. Temperatures were read on a Leeds and Northrup portable potentiometer, employing a calibrated chromel-alumel thermocouple positioned in the block near the sample.

Samples whose melting points were to be determined were prepared by the methods described in the Materials Section; i.e., either by the direct combination of the elements in the correct proportion to give the desired atom ratio of iodine to gallium, or by the reduction of the triiodide-iodine complex by gallium. In the latter case, the iodine

to gallium atom ratio was determined by analysis of the sample.

The melting points of samples lower in iodine content than $GaI_{2.3}$ varied markedly with the thermal history of the sample. The higher the temperature from which the sample was quenched, the lower was the temperature at which it melted. In addition, these samples when cooled rapidly formed glasses which showed little tendency to crystallize at room temperature, but which could be crystallized on warming to about 100° for a few minutes.

Because of these difficulties, the following procedure was adopted for the visual determination of the melting points. Fused samples were heated at a given temperature for at least four hours, quenched with an air blast, and if necessary heated briefly at 100° to crystallize them. They were then inserted into the furnace, which had been previously heated to just below the expected melting point, and heated at the rate of about one degree per minute. The temperature at which the last crystals melted was noted. This procedure was repeated, the fused sample being equilibrated at successively lower temperatures, until a maximum melting point was obtained when the sample had been quenched from one to five degrees above this temperature. At this melting point, the last crystals were in true equilibrium with the melt.

The points so obtained were reproducible to within one degree and showed no drift with time.

B. Solubility of Gallium in Halide Systems

The following procedures were used to determine the apparent solubility of gallium metal in the halide systems.

1. In the chloride and iodide systems, the metal and gallium trihalide were equilibrated at 180° and 267°, respectively, for four days and the quenched salt phase was analyzed.
2. In the bromide system, weighed amounts of metal and the tribromide were equilibrated for four days at 170°, and the loss in weight of gallium determined.
3. In the gallium trichloride-aluminum chloride system, a weighed amount of gallium was equilibrated for four days at 190° with a three to one mole mixture of aluminum chloride and gallium trichloride, and the loss in weight of metal determined. A similar procedure was used to determine the solubility of gallium in aluminum trichloride.

C. Cryoscopic Measurements

Molecular weights of gallium dichloride and gallium(I) tetrachloroaluminate in benzene were determined by a cryoscopic procedure employing a thermistor as the temperature-sensing element. The use of thermistors in resistance thermometry has been described by Johnson and Kraus (28), and the application of thermistors to cryoscopic measurements has been presented by McMullan and Corbett (29). A discussion of the calibration and accuracy of the thermistor in cryoscopic measurements, together with a derivation of equations relating resistance to concentration, is included in the Appendix.

The change in thermistor resistance, corresponding to the freezing point depression, was determined by a Wheatstone bridge. The thermistor used was a Carbaloy type D-102, with a resistance of about 2300 ohms and a temperature coefficient of resistance of four percent per degree at 5°. The bridge included two 1000 ohm standard resistors for the fixed arms, a Leeds and Northrup 2420-d galvanometer for the detector, and a bank of four parallel 1.5 volt dry cells in series with a 500 ohm resistor for the current source. For the variable resistance, two decade boxes (1, 10, 1000 ohm steps) were used in parallel in order to increase the sensitivity of

the bridge without the use of decades with smaller resistance increments.

The design of the glass cryoscopic cell is illustrated in Figure 2. The total volume of the cell was approximately 200 ml., one-half of which was filled with solution. The cell was surrounded by jacket C which could be evacuated during the freezing process to control the rate of cooling. Standard tapers 1, 2 and 3 were lubricated with a stopcock grease ("Nonaq", Fisher Scientific Co.) which was insoluble in nonpolar organic solvents. The solution could be stirred by glass-encased bar magnet B actuated by a magnetic stirrer placed beneath the jacketed cell. The thermistor was positioned at the bottom of thin-walled tube A, and the bottom inch of the tube filled with petroleum ether to provide the thermistor with better thermal contact to the solution. The use of water-miscible liquids here caused erratic results in the resistance measurements, apparently due to conduction between the lead wires.

The vacuum system used in the preparation of dry benzene is illustrated in Figure 3. The volumes of A and D were 1000 ml., those of C and B were 500 ml., and that of E was 250 ml. Each flask in the lower tier contained calcium hydride. Mercury float valves I through IX were used where prolonged

Figure 2. The Cryoscopic Cell

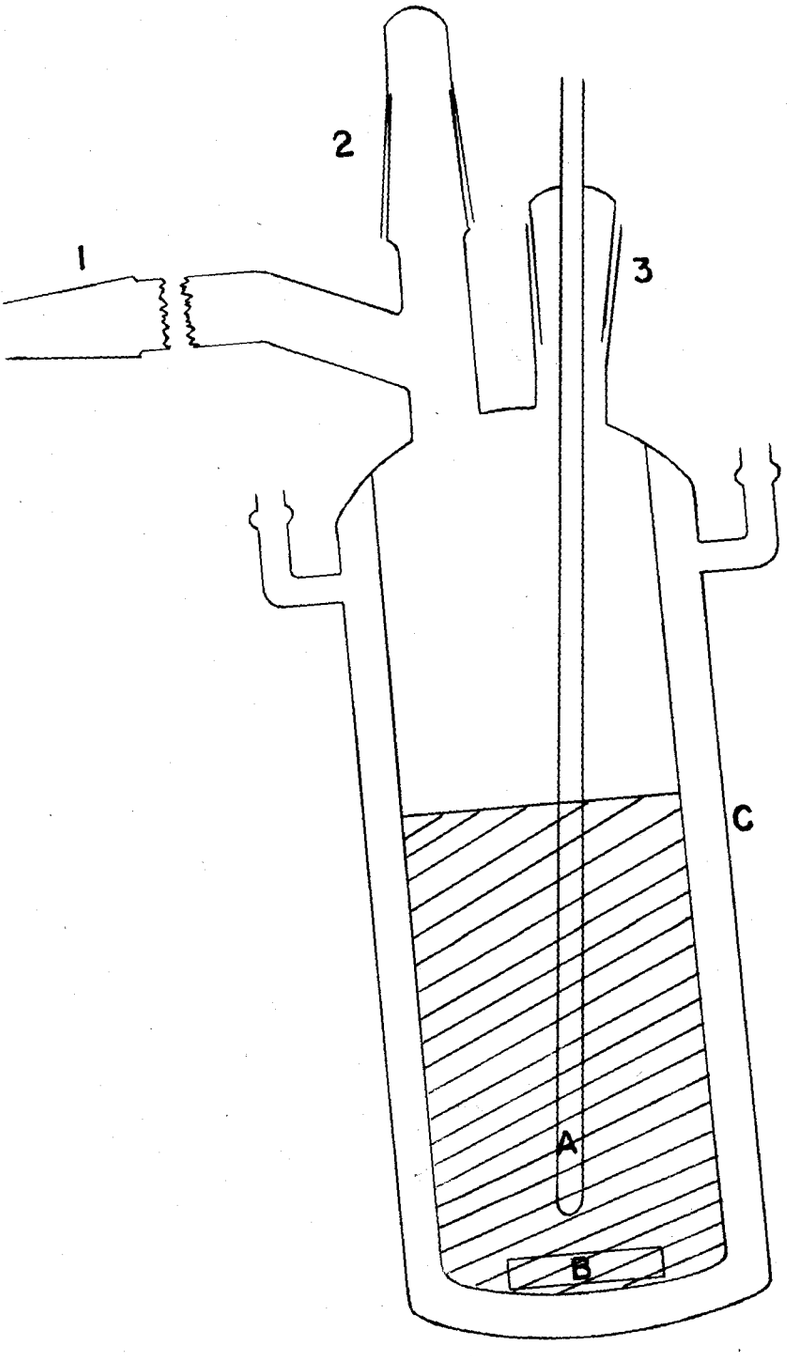
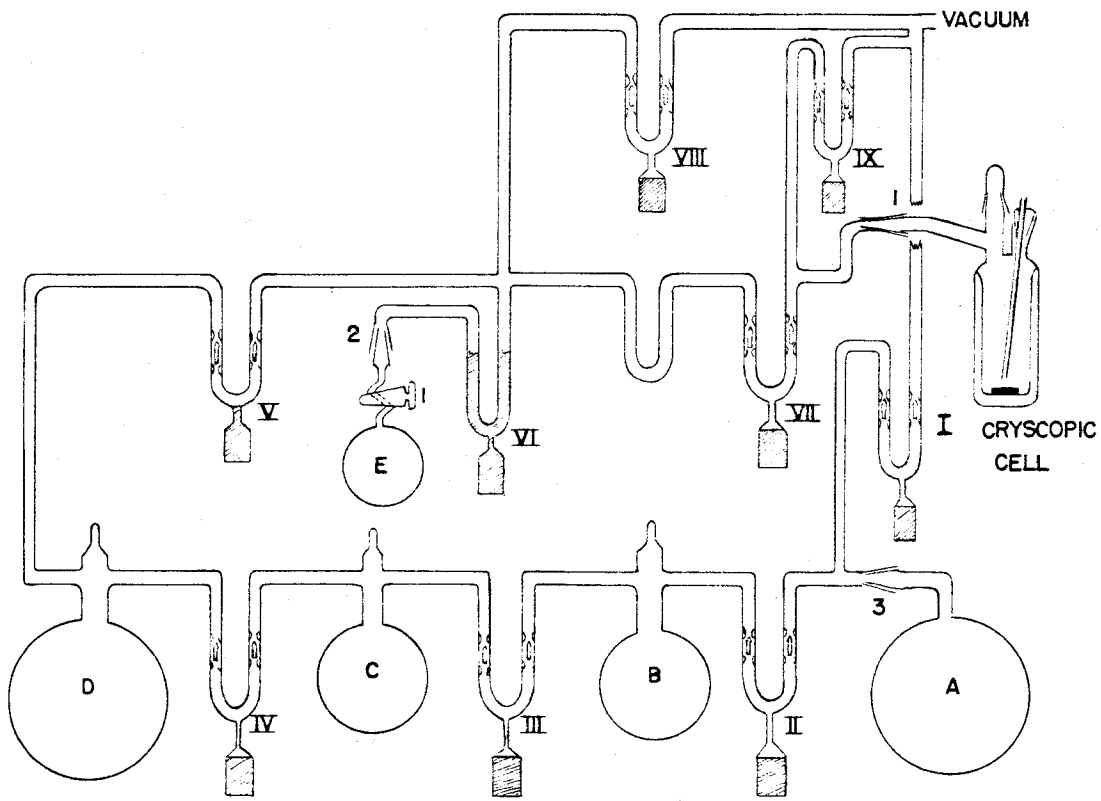

1
2
3
A
B
C

Figure 3. Vacuum System for Solvent Transfer Operations


VACUUM
VIII
IX
I
2
1
V
VI
VII
I
CRYSCOPIC
CELL
E
3
D
C
B
A
IV
III
II

contact with benzene occurred. Stopcock 1 and the detachable standard tapers 1, 2 and 3 were lubricated with "Nonaq".

In order to introduce benzene into the system, valves I and II were closed, and flask A, containing approximately 500 ml. of benzene, was attached at standard taper 3. The flask was immersed in a dry ice-acetone bath to freeze the benzene and evacuated through valve I. The benzene was stepwise distilled through the drying system and subsequently stored over calcium hydride in flask D. Approximately 100 ml. of benzene was condensed into flask E and, with stopcock 1 and valve VI closed, the flask was detached and weighed to the nearest milligram. Flask E was replaced and the system evacuated. The solvent was condensed into the cryoscopic cell and the cell isolated by closing valves VII and IX. The amount transferred was then determined by reweighing flask E.

The benzene was permitted to slowly melt, the rate being controlled by the gas pressure in the vacuum jacket. After the system had reached room temperature, the thermistor was positioned in tube A, and the cell immersed in an ice bath. With the jacket evacuated, the cooling rate for approximately 90 g. of benzene was about 0.05° per minute with a temperature difference of five degrees. Three or four resistance measurements corresponding to the freezing point of pure

benzene were made, and these values averaged. Dry argon was then admitted into the evacuated cell, and a weighed quantity of salt added through standard taper 2 (Figure 2) from a glass capsule which had been filled in the dry box under an atmosphere of dry helium. During the additions, the solution was protected from the air by the blanket of heavy argon, and the salt, in the inverted capsule, by light helium. The cap was then replaced on standard taper 2, and the cell again evacuated. Any solvent lost in the evacuation was condensed in a trap and subsequently transferred to flask E and weighed. The solvent was again frozen and the resistance measurement made. By successive additions of salt, the freezing points were obtained at points over an extensive concentration range.

During the freezing point measurements, a constant resistance plateau was obtained for two to four minutes after a supercooling of a few tenths of a degree. If greater supercooling was observed, the solutions were warmed until only a few seed crystals remained, then recooled to the freezing point, and the measurements repeated. Balance was achieved in a closed circuit so that bridge current heating the thermistor (about one milliwatt) would reach a steady state. The solution freezing points determined by this procedure represented the actual equilibrium between the solution

at the specified concentration and the solid benzene, within the accuracy of the thermistor measurements. As discussed in the Appendix, the average deviation in the concentrations determined cryoscopically was 2.2×10^{-4} molality units in the range from zero to one-tenth molal. The average deviation of the corresponding temperature measurements would be 1.1×10^{-3} degrees.

It is felt that the apparatus described has the following notable features:

1. The solvents used can be weighed and transferred *in vacuo* without contamination from moisture or stopcock greases.
2. The relatively large temperature coefficient of thermistor resistance enables accurate measurements of freezing point depression with a simple bridge circuit. In addition, the thermistor responds rapidly to temperature changes as a result of its small mass.
3. Cryoscopic measurements with a thermistor become increasingly more accurate at low temperatures because of the increasingly negative temperature coefficient of resistance.

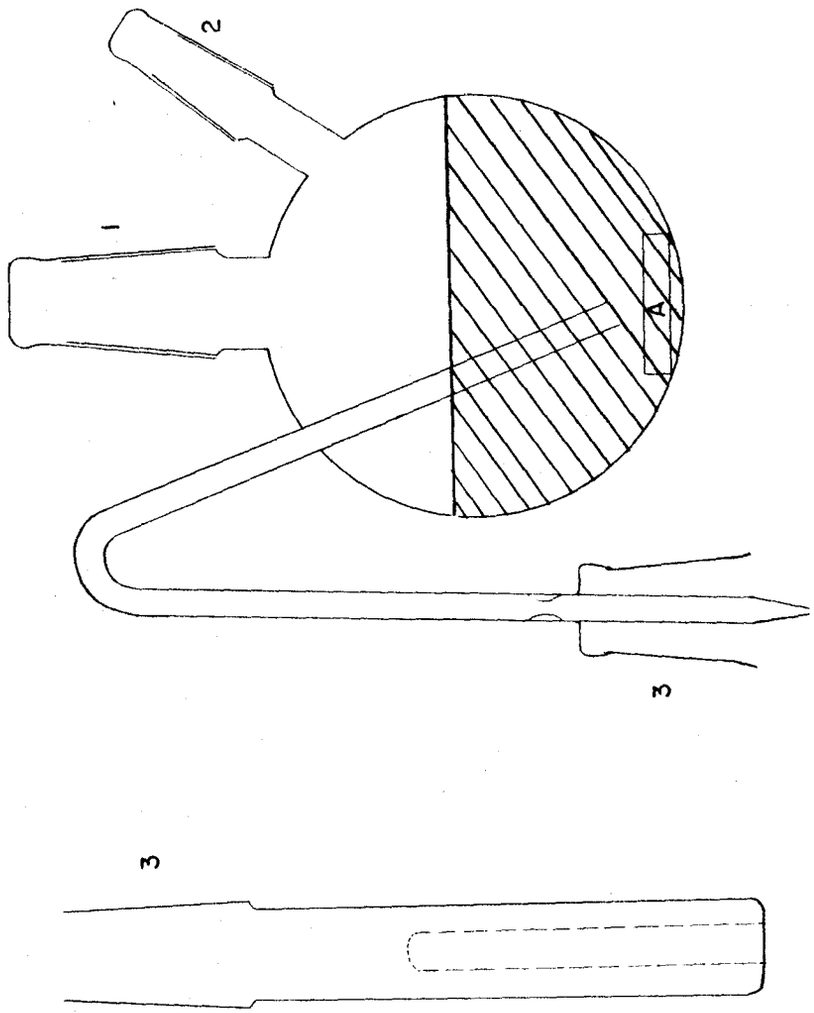
D. Dielectric Constant Measurements

The dielectric constants of solutions of gallium dichloride and of chlorobenzene in benzene were determined by a resonance method using a Sargent Chemical Oscillometer Model V with cell compensation. Reference is made to the authoritative book by Smyth (30) for a description of the method and to the literature published by the manufacturers (31) for the description of the electronic circuit of the apparatus. The dielectric cell shown in Figure 4 A had an annular sample chamber between concentric, externally applied metal coated areas. The cell was calibrated with benzene as a dielectric standard, and the calibration checked prior to each measurement. Values of the dielectric constant of the solutions were determined relative to benzene by measuring the increase in cell capacitance when benzene was replaced by the solutions. High precision has been attributed to the dielectric constants determined by this differential procedure (30).

The cell holder was supported on an insulating block and enclosed by a Dewar flask. A spiral of copper tubing was placed around the cell and connected through the support to a constant temperature bath. Water from the bath was circulated through the copper tubing by a suction pump. A

Figure 4. A. Oscillometer Cell

B. Apparatus for the Preparation of Benzene Solutions of Gallium Dichloride


2
1
A
3
B
3
A

mercury thermal regulator maintained the temperature of the bath at 25 ± 0.02° by controlling an infrared heat source. A calibrated iron-constantan thermocouple was used to determine when the dead air space surrounding the cell had reached thermal equilibrium with the water bath.

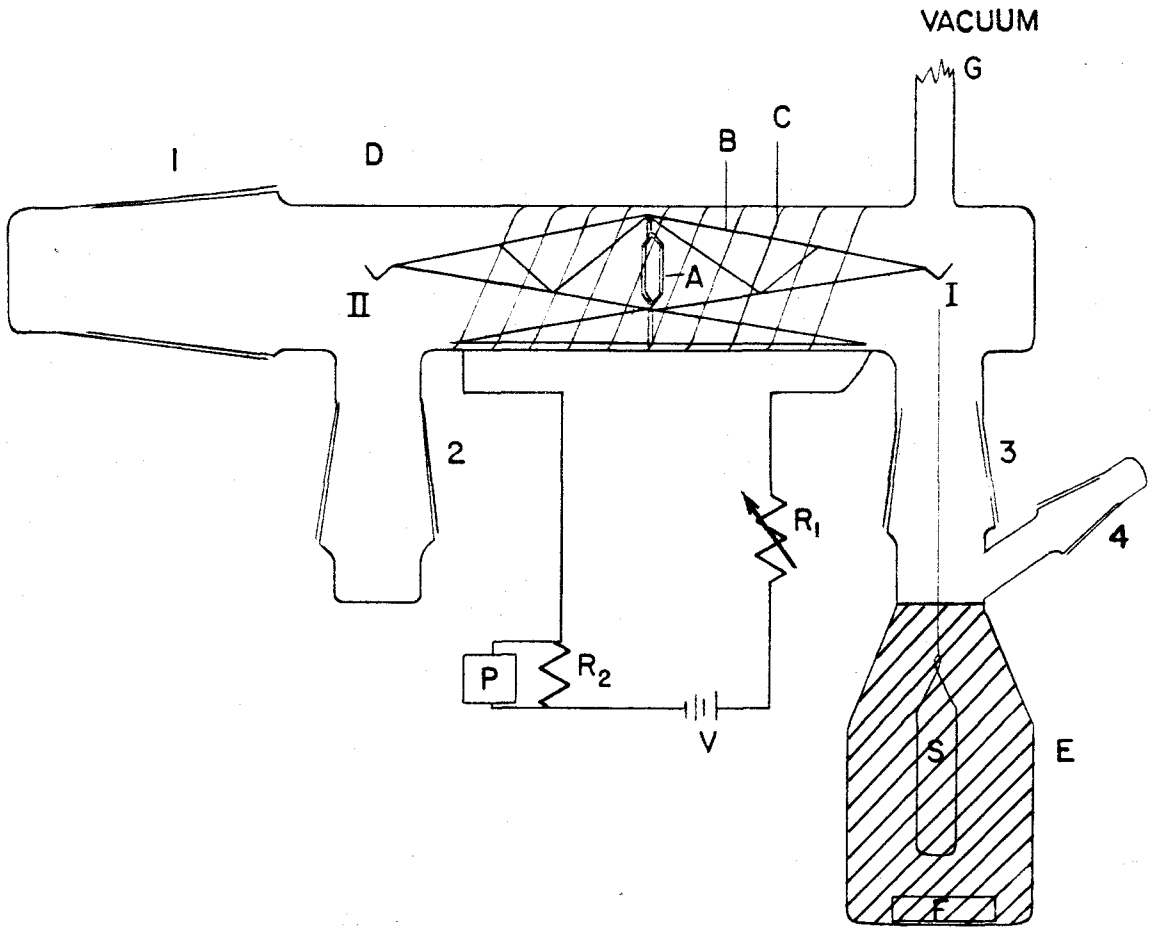
Measurements were made on a series of five solutions ranging in mole fraction solute from 0.0001 to 0.0005 for Ga_2Cl_4 and from 0.001 to 0.03 for chlorobenzene. The chlorobenzene solutions were prepared by mixing weighed amounts of the dried components in the dry box. For the preparation of the gallium dichloride solutions, the apparatus shown in Figure 4 B was attached to the solvent drying system (Figure 3) by means of standard taper 1. The system was thoroughly evacuated and then filled with dry argon. Gallium dichloride was added to the system through standard taper 2, and the system re-evacuated. Benzene was condensed onto the salt and the solution stirred with bar magnet A. The solution was transferred into the sample cell attached at standard taper 3 by warming the solution until the vapor pressure of the benzene was sufficient to force the solution from the reservoir. The cell was then sealed from the flask at the indicated constriction above standard taper 3. The dielectric constant measurements were made after the sample had attained thermal equilibrium with the dead air space. The

weights of the solutions were determined by difference, and the concentrations of gallium dichloride determined by gallium analyses.

E. Solution Density Measurements

Density data were obtained for solutions of gallium dichloride in benzene by a differential buoyancy method employing a magnetically compensated balance of the type described by Edwards and Baldwin (32). The design of the balance is shown in Figure 5. The balance arm B was constructed of silica and suspended on two fine horizontal silica fibers attached to a silica support. From the weighing arm of the balance at I, a sinker S was suspended below the surface of the solution. Small platinum wire tares were hung at II to counterbalance the weight of the sinker. At the suspension point, a small quartz-encased Alnico magnet A was mounted vertically. The balance case D was wrapped with approximately 500 turns of #28 insulated copper wire to form a solenoid, the field of which acted on the magnet. For a reference point, the position of pointer II was observed with a fixed telescope. Balance was achieved by varying the current passed through the solenoid until the pointer returned to the reference point. The current was determined

Figure 5. Solution Density Balance


VACUUM
G
I
D
B
C
A
II
I
2
3
4
R_1
P
R_2
V
S
E
F

from the voltage drop measured across the standard resistor R_2.

Tube G was connected to the solvent drying system and a weighed amount of benzene condensed into container E. Through standard taper 4, a weighed quantity of gallium dichloride was added from an ampule which had been filled in the dry box. The solution was stirred from below by a magnetic stirrer, and then surrounded by a large Dewar flask through which water thermostated at 25 ± 0.02° circulated. Measurements were made after the solutions had reached thermal equilibrium with the water bath.

Calibration of the apparatus was obtained by measuring the current necessary to balance known weights suspended from II. The plot of milligrams weights against milliamperes current in the solenoid was linear throughout the range used in the study. Checks were made to determine whether the weight of the load changed the calibration of the balance. When one gram weights were placed on the arm of the balance, no change in the calibration could be detected. The reproducibility of the balance used was 0.1 milligram, which corresponds to less than 0.00002 g/cm^3 uncertainty in the density. The sensitivity of the balance was about 1.3 milligrams per milliampere. The differential densities relative to benzene were calculated from the increment of current necessary to reestablish balance.

F. X-Ray Powder Diffraction Measurements

All X-ray powder diffraction patterns were made with a North American Phillips diffraction unit using radiation emitted by a copper target and filtered through a nickel foil. The operating conditions were: 45 kv. tube voltage, 18 ma. filament current and exposure periods of eight to twelve hours depending on the sample. Diffraction lines were measured on a light table and their intensities estimated visually. The weighted average value of the wave lengths of the $K\alpha_1$ and $K\alpha_2$ copper radiation (1.5418 $\mathring{A}$) was used in the calculation of the interplanar spacings. None of the diffraction data obtained could be indexed with the use of Bunn Charts.

G. Raman Measurements

Benzene solutions of gallium dichloride and of silver tetrachlorogallate were prepared for Raman spectra examinations by a procedure similar to that used in the dielectric constant studies. The concentrations of both solutions were approximately one mole percent based on the formula weights Ga_2Cl_4 and $Ag(GaCl_4)$. The spectra were recorded photographically with a Lane-Wells high-speed Raman spectrograph

(#40-A6) employing a #60-A2 mercury excitation unit. Typical exposures were made for two hours, with a slit width of 200 microns and a 20 ampere excitation current. Five spectra were recorded for each solution, and the photograph with the highest line-to-background intensity ratio selected for the frequency measurements. The frequencies were determined by direct measurements on the plates with a visual comparator. A maximum absolute error of five cm^{-1} was estimated for the measurements; comparative measurements were probably accurate to one cm^{-1}.

H. Analytical Methods

1. Gallium. In analyses of solid samples, gallium was determined gravimetrically as the tris-5,7-dibromo-8-hydroxyquinolate (33). Average errors less than 0.1 percent were obtained on analysis of standard solutions prepared by dissolving gallium in perchloric acid. In analyses of solutions from the dielectric constant measurements, gallium tris-5,7-dibromo-8-hydroxyquinolate was extracted from aqueous solution into chloroform and the determination made by a spectrophotometric method*. The accuracy of the method was approximately three percent.

*The author is indebted to the Analytical Service Group of Ames Laboratory for the spectrophotometric determinations.

2. Halogens. Chloride and bromide were determined by precipitation and weighing of the silver salts. Iodide was determined by a silver titration using eosin as the indicator.

In order to prevent the loss of hydrogen halide by hydrolysis, all solid gallium halide samples were opened and transferred in the dry box. The salts were dissolved in evacuated containers by the admission of 0.1 N sulfuric acid. Gallium dihalides produced metallic gallium on dissolution, along with a flocculent brown or orange-brown precipitate from which hydrogen evolved. Compositions near $GaI_{1.2}$ dissolved with the formation of a similar solid but without the precipitation of metal. Any metal produced was dissolved in concentrated nitric acid, and the solution combined with the rest of the sample. The aqueous solutions were heated for several hours to ensure complete oxidation of gallium to the trivalent state. The halogen to gallium atom ratios were determined rather than the elemental weight percentages, since the preparative methods used insured the absence of significant amounts of foreign elements. Samples that were submitted for spectrophotometric analyses were similarly treated.

IV. EXPERIMENTAL RESULTS

A. General Properties of Gallium Dihalides

The three gallium dihalides are crystalline compounds; the chloride and bromide are white, while the iodide is yellow. The melting point determined for the chloride is 171 ± 1°, as compared to the value 170.5° reported by Laubengayer and Schirmer (17). The bromide is observed to be dimorphic; the form stable at room temperature melts at 154°, while the high temperature form melts at 162°. Attempts to determine the transition point gave inconclusive results. The solid-solid phase transition reported to occur in gallium dichloride (17) was not found in this work. The apparent transition observed was perhaps due to the initiation of crystallization in the supercooled glass. The melting point of the diiodide is 211°. However, this melting point is strongly dependent on the thermal history of the compound. For example, heating gallium diiodide at 250° for a few hours causes the melting point to drop several degrees, while allowing the sample to stand for two weeks at room temperature results in a melting point of 229°. The value 211°, determined by the method described in Section III, is the true melting point, i.e., the temperature at which the last

crystals are in equilibrium with the melt. The melting points of gallium dichloride and gallium dibromide are not dependent on previous thermal treatment.

If gallium dichloride is heated to 200° to 250° extensive disproportionation is observed. Gallium trichloride volatilizes from the melt and metallic gallium separates. Similarly, if gallium dibromide or gallium diiodide is heated above 250°, volatilization of the trihalide is again observed, but the separation of metallic gallium does not occur unless large amounts of the trihalide are removed. In the chloride system, solidification of the melt remaining after the disproportionation produces a mixture that has a greyish appearance, due to droplets of dispersed gallium. In contrast, in the bromide and iodide systems, no gallium separates from the salt upon crystallization of the melts.

As was pointed out in the Introduction, gallium dichloride is diamagnetic. The diamagnetism of the dibromide and the diiodide was also established by qualitative examination with a Gouy balance.*

X-Ray powder diffraction data for gallium dichloride and gallium diiodide are given in Tables 1 and 2, respectively.

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*The author is indebted to Dr. Wilford Hansen for his assistance during this examination.

Table 1. X-Ray Powder Diffraction Data for Gallium Dichloride

d(obs.) Å	Intensity	d(obs.) Å	Intensity
6.86	3	1.817	1
5.77	2	1.793	1
4.82	5	1.752	1
3.73	10	1.697	2
3.42	1	1.667	4
3.21	5	1.610	1
3.08	2	1.597	1
2.95	1	1.559	1
2.91	4	1.539	1
2.85	1	1.510	1
2.78	6	1.499	2
2.50	4	1.478	1
2.45	1	1.431	1
2.39	1	1.395	1
2.33	4	1.369	1
2.27	2	1.338	1
2.17	3	1.317	1
2.10	1	1.273	1
2.01	1	1.236	1
1.925	3	1.196	1
1.858	3		

Table 2. X-Ray Powder Diffraction Data for Annealed Gallium Diiodide

d(obs.) Å	Intensity	d(obs.) Å	Intensity
7.27	4	1.874	5
6.27	4	1.815	5
5.68	4	1.752	2
3.66	6	1.700	2
3.50	10	1.622	4
3.28	7	1.544	1
3.07	9	1.489	1
2.89	7	1.454	1
2.76	3	1.337	1
2.64	4	1.320	1
2.50	2	1.281	3
2.41	2		
2.21	2		
2.14	2		
2.10	2		
2.01	4		
1.975	4		

The relative intensity values are based on the strongest line being assigned the value of 10.

B. Solubility of Gallium in Fused Halide Systems

In Table 3 are presented the data for the solubility of gallium in various halide systems. It should be pointed out that the term solubility as used here does not imply a simple solution of metal in the fused systems, but rather solution with reduction of the tripositive metal to a lower oxidation state. For consistency, solubility results are listed as the mole ratio of dissolved gallium to the indicated trihalide. The two methods used to determine these solubilities were the direct analysis of the quenched salt phase (Method A) and loss of weight of metallic gallium upon solution in the molten salt (Method B). The colors listed in the last two columns are those of the liquid at the equilibration temperature and of the solid at room temperature.

C. Phase Diagram of the Gallium-Gallium Triiodide System

The experimental temperature-composition data for the gallium-gallium triiodide system are given in Table 4 and

Table 3. Solubility of Gallium in Fused Halide Systems

Systems	Equilibration Temp. °C	Dissolved Metal Mole Ratio		Method	Color	
		$Ga:GaX_3$[a]	$Ga:AlCl_3$		Liquid	Solid
$Ga-GaCl_3$	180	0.529	----	A	colorless	gray
$Ga-GaBr_3$	170	0.654	----	A	pale green	white
$Ga-GaI_3$	267	1.52	----	A	dark red	yellow
$Ga-GaCl_3-AlCl_3$ ($AlCl_3:GaCl_3>3:1$)	190	1.99	----	B	colorless	white
$Ga-AlCl_3$	190	----	0.000	B	colorless	white

[a] Ga_2X_4 corresponds to a $Ga:GaX_3$ mole ratio of 0.500; X denotes either chlorine, bromine or iodine.

Table 4. Temperature-Composition Data for Gallium-Gallium Triiodide System

I:Ga Atom Ratio	Temperature °C	
	Liquidus	Eutectic
3.00[a]	214	-
2.80[a]	210	-
2.61[a]	199	-
2.36[a]	159	-
2.30[a]	175	160
2.20[a]	190	161
2.10[a]	203	-
2.00[a]	211	-
1.95[a]	209	205
1.90[a]	207	205
1.86[a]	218	-
1.687[b]	239	205
1.398[b]	256	206
1.186	267	-

[a]Calculated from weights of components.

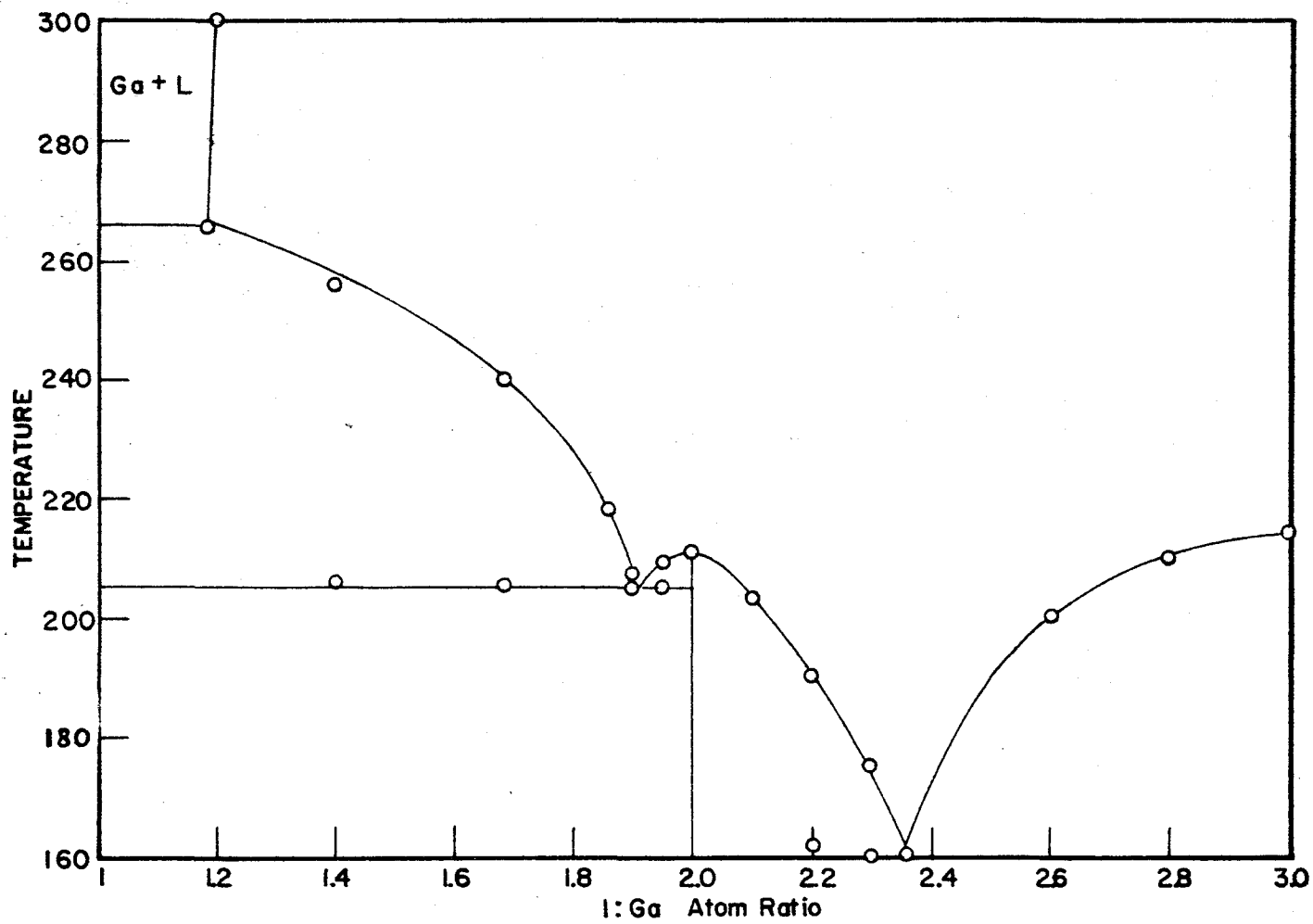
[b]Determined by chemical analysis.

Figure 6. The lowest value of the iodide to gallium atom ratio (1.19) corresponds to the composition of the metal saturated system and is calculated from the value listed in Table 3. Approximate eutectic temperatures are recorded as the points at which the first premelting was observed. These are in good agreement with those temperatures determined from the liquidus curve intersections (204° and 160°). The phase boundary between the metal and salt was established by analyses of salt mixtures quenched from 500°, 300° and 267°. The corresponding salt compositions are, respectively, $GaI_{1.20}$, $GaI_{1.21}$ and $GaI_{1.19}$. The melting points of the triiodide, diiodide and monoiodide are, respectively, 214° [literature: 210° (18) and 213.5° (34)], 211° and 271° (extrapolated).

D. Gallium(I) Iodide

The phase diagram of the gallium-gallium triiodide system indicates that gallium monoiodide does not have sufficient stability above 267° to exist as the pure phase but only as a liquid containing 10 per cent Ga_2I_4 in equilibrium with the metal. Below the liquidus curve, red crystals of gallium monoiodide separate from the melt. Disproportionation in crystalline gallium monoiodide apparently does not occur.

Figure 6. Phase Diagram of the Gallium-Gallium Triiodide System


300
280
260
240
220
200
180
160
Ga + L
TEMPERATURE
1
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
1: Ga Atom Ratio

The isolation of gallium monoiodide was achieved by a benzene extraction of gallium diiodide from the solid mixture containing 90 mole percent GaI. The residue analyzed $GaI_{1.06}$.

X-Ray powder diffraction patterns obtained for the three gallium iodides are shown in Figure 7. The complete data for the diiodide have been listed in Table 2, while those for the monoiodide and triiodide* are listed in Tables 5 and 6. The uniqueness of the three compounds is clearly demonstrated.

E. Gallium(I) Tetrachloroaluminate

Although the experimental mole ratios showed that the reaction

$$4GaCl_3 + 3Al = 3Ga(AlCl_4) + Ga \qquad (4)$$

produced a compound with the composition $GaAlCl_4$, an unambiguous assignment of oxidation states to gallium and aluminum was not possible from these data alone. Alternately, $Al(I)[Ga(III)Cl_4]$ could be formed by a reaction with the same stoichiometry. However, calculations based on estimated

*A comparison of these data with the powder diffraction data listed for aluminum iodide (35) reveals that the two compounds are isomorphous.

Figure 7. X-Ray Diffraction Patterns of GaI_3, GaI_2 and GaI

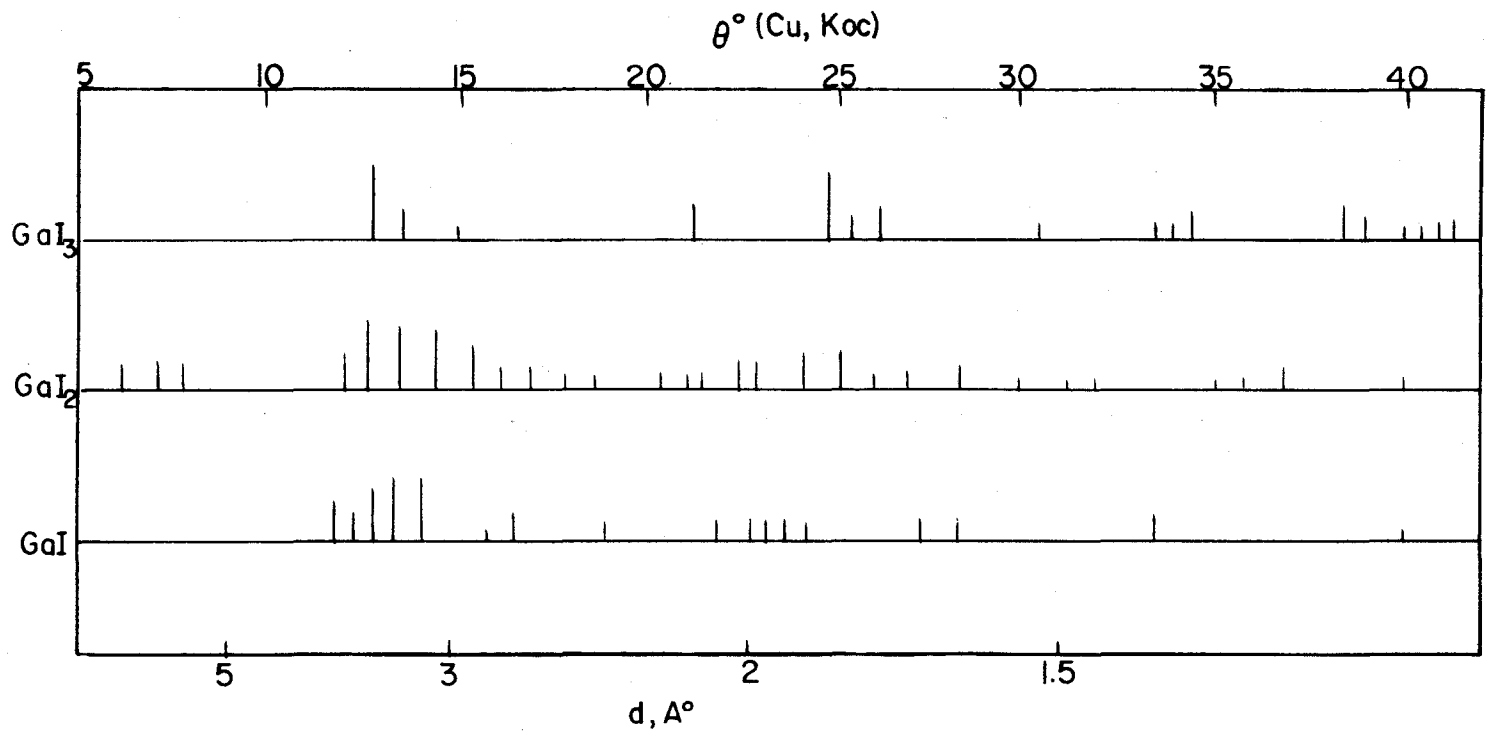

θ° (Cu, Koc)
5
10
15
20
25
30
35
40
GaI3
GaI2
GaI
5
3
2
1.5
d, A°

Table 5. X-Ray Powder Diffraction Data for Gallium Monoiodide

d(obs.) Å	Intensity
3.76	6
3.62	5
3.47	7
3.32	9
3.16	10
2.94	1
2.82	1
2.71	5
2.37	3
2.06	2
1.985	3
1.953	3
1.917	3
1.880	2
1.869	2
1.677	3
1.632	4
1.397	3

Table 6. X-Ray Powder Diffraction Data for Gallium Triiodide

d(obs.) Å	Intensity
3.46	10
3.03	5
2.95	2
2.15	6
2.11	5
1.829	9
1.792	3
1.739	4
1.520	2
1.394	2
1.379	1
1.356	4
1.237	10
1.221	3
1.171	1
1.160	1
1.142	1

thermodynamic values tabulated by Brewer et al. (36) indicated that the free energy of formation of Al(I)[Ga(III)Cl_4] by the above reaction was unfavorable by approximately 50 kcal. Experimentally, these calculations were verified by the metal solubility data for the Ga-$AlCl_3$ system. These results (Table 3) showed that reduction of $AlCl_3$ by gallium was negligible and that the disproportionation of aluminum(I) was essentially complete. Accordingly, the compound was formulated as Ga(I)[Al(III)Cl_4].

Gallium(I) tetrachloroaluminate forms colorless crystals which melt at 175 ± 1°. Single transparent crystals can be grown by maintaining the melt at the freezing point for several days. X-Ray powder diffraction data for the compound are listed in Table 7.

F. Cryoscopic Results

The experimental data obtained from the freezing point measurements were values of the thermistor resistance at various stoichiometric molalities, m_s*. The measurements as applied to apparent molecular weight determinations of

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*These concentrations in the case of gallium dichloride were based on the formula weight of Ga_2Cl_4 and in the case of gallium(I) tetrachloroaluminate on the formula weight of $GaAlCl_4$.

Table 7. X-Ray Powder Diffraction Data for Gallium(I) Tetrachloroaluminate

d(obs.) Å	Intensity	d(obs.) Å	Intensity
5.06	2	2.45	3
4.87	1	2.40	0.5
4.60	4	2.34	1
4.18	3	2.23	4
3.87	5	2.22	1
3.73	2	2.15	1
3.58	2	2.04	1
3.39	1	1.964	2
3.23	2	1.895	2
3.12	3	1.860	1
3.05	3	1.744	1
2.94	10	1.726	1
2.89	1	1.681	1
2.84	3	1.655	1
2.76	1	1.621	1
2.73	1	1.492	1
2.67	6	1.458	1
2.53	7	1.405	1

gallium dichloride and of gallium(I) tetrachloroaluminate in benzene solutions are shown in Table 8. The effective solution molality, m_e, was calculated from the resistance measurement by the method described in the Appendix. At each stoichiometric concentration, the apparent molecular weight was determined from the effective molality and the weight of the solute used. A plot of apparent molecular weight *vs.* concentration for the gallium dichloride system is shown in Figure 8. The extrapolated value for the molecular weight at infinite dilution is 280 ± 5, which compares favorably with the value 281.2 for the formula weight of Ga_2Cl_4.

G. Dielectric Constant Data

The experimentally determined dielectric constant values for solutions of gallium dichloride and of chlorobenzene in benzene are given in Table 9. These data are represented graphically in Figure 9, together with similar data for the solution of silver perchlorate in benzene determined by Hooper and Kraus (38). The chlorobenzene data shown in the figure were obtained by linear extrapolation from the experimental values since the lowest concentrations at which reliable measurements could be made were in a range

Table 8. Effective Concentrations and Apparent Molecular Weights of Gallium Dichloride and of Gallium(I) Tetrachloroaluminate in Benzene

r_o ohms	r ohms	Δr ohms	Stoichiometric Concentration $m_s \times 10^2$	Effective Concentration $m_e \times 10^2$	Apparent Molecular Weight
			Gallium Dichloride		
2293.30	2295.21	1.91	0.4197	0.386	305.8
	2296.96	3.65	0.8378	0.737	319.5
	2301.73	8.43	2.311	1.700	382.4
	2306.21	12.91	4.058	2.601	438.8
	2309.38	16.08	5.530	3.238	480.2
	2314.42	21.12	8.215	4.248	543.8
2296.62	2302.56	5.94	1.528	1.197	358.9
	2305.46	8.84	2.571	1.780	398.0
	2307.42	10.80	3.270	2.174	422.9
	2309.83	13.21	4.211	2.658	445.5
2300.03	2305.12	5.09	1.240	1.023	340.8
			Gallium(I) Tetrachloroaluminate		
2192.18	2196.29	4.11	1.284	0.868	352.8
	2200.12	7.94	2.892	1.674	411.9
	2203.38	11.20	4.412	2.360	445.9
	2205.77	13.59	5.773	2.862	481.1

Figure 8. Apparent Molecular Weight of Gallium Dichloride in Benzene

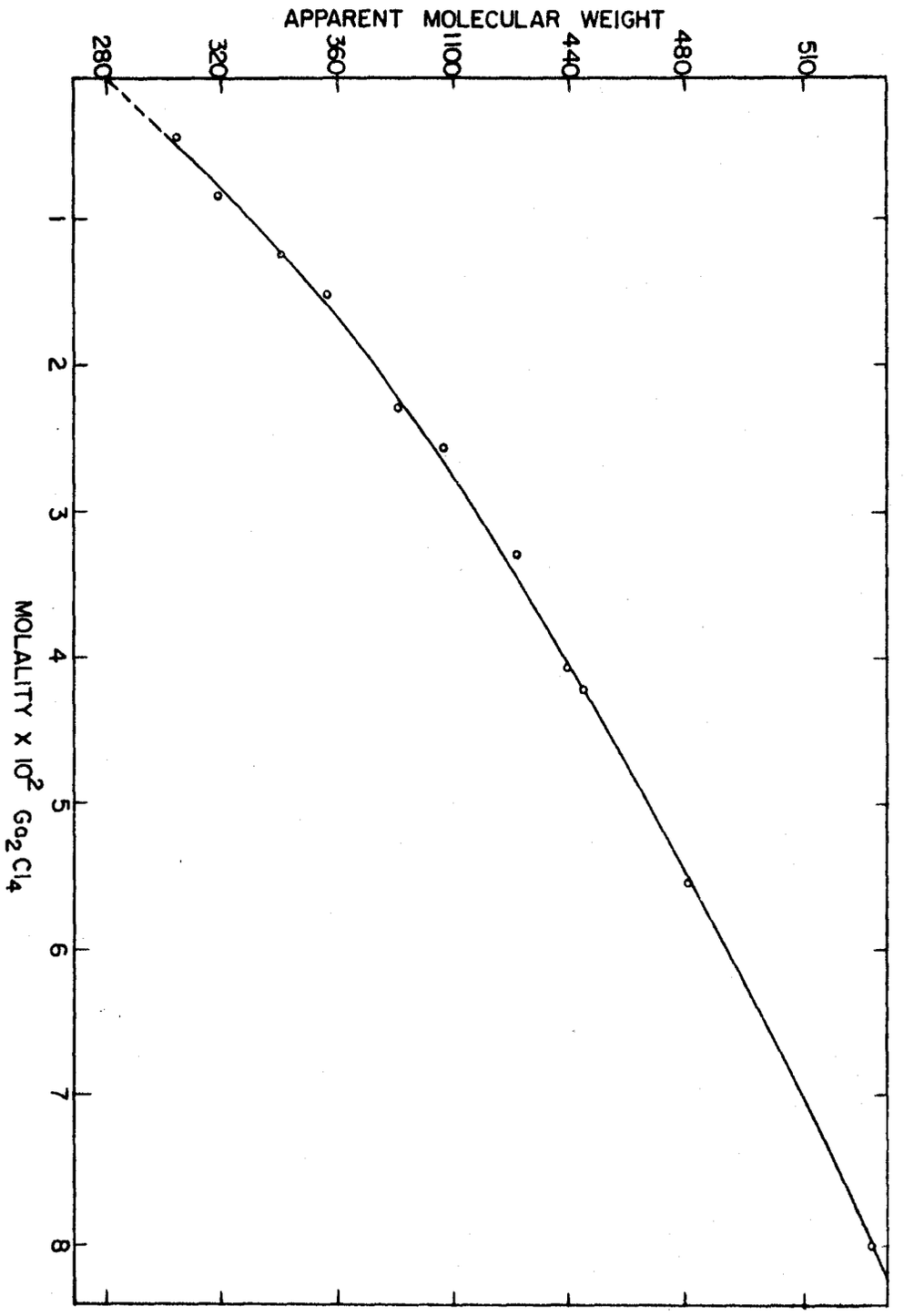

APPARENT MOLECULAR WEIGHT
280
320
360
1100
440
480
510
1
2
3
4
5
6
7
8
MOLALITY X 10^2 Ga_2Cl_4

Table 9. Dielectric Constant Data for Benzene Solutions of Gallium Dichloride and of Chlorobenzene at 25°

Mole Fraction x 10^4	$\Delta\epsilon$ x 10^2	ϵ
	Gallium Dichloride[a]	
0.00	0.00	2.2722[b]
0.95[c]	0.99	2.2821
1.20[c]	1.30	2.2852
2.73[c]	2.91	2.3013
3.42[c]	3.62	2.3084
5.05[d]	4.90	2.3212
	Chlorobenzene	
0.00	0.00	2.2722[b]
14.5[d]	0.39	2.2761
36.2[d]	1.12	2.2834
180.7[d]	5.57	2.3279
229.6[d]	7.11	2.3433
331.7[d]	10.47	2.3769

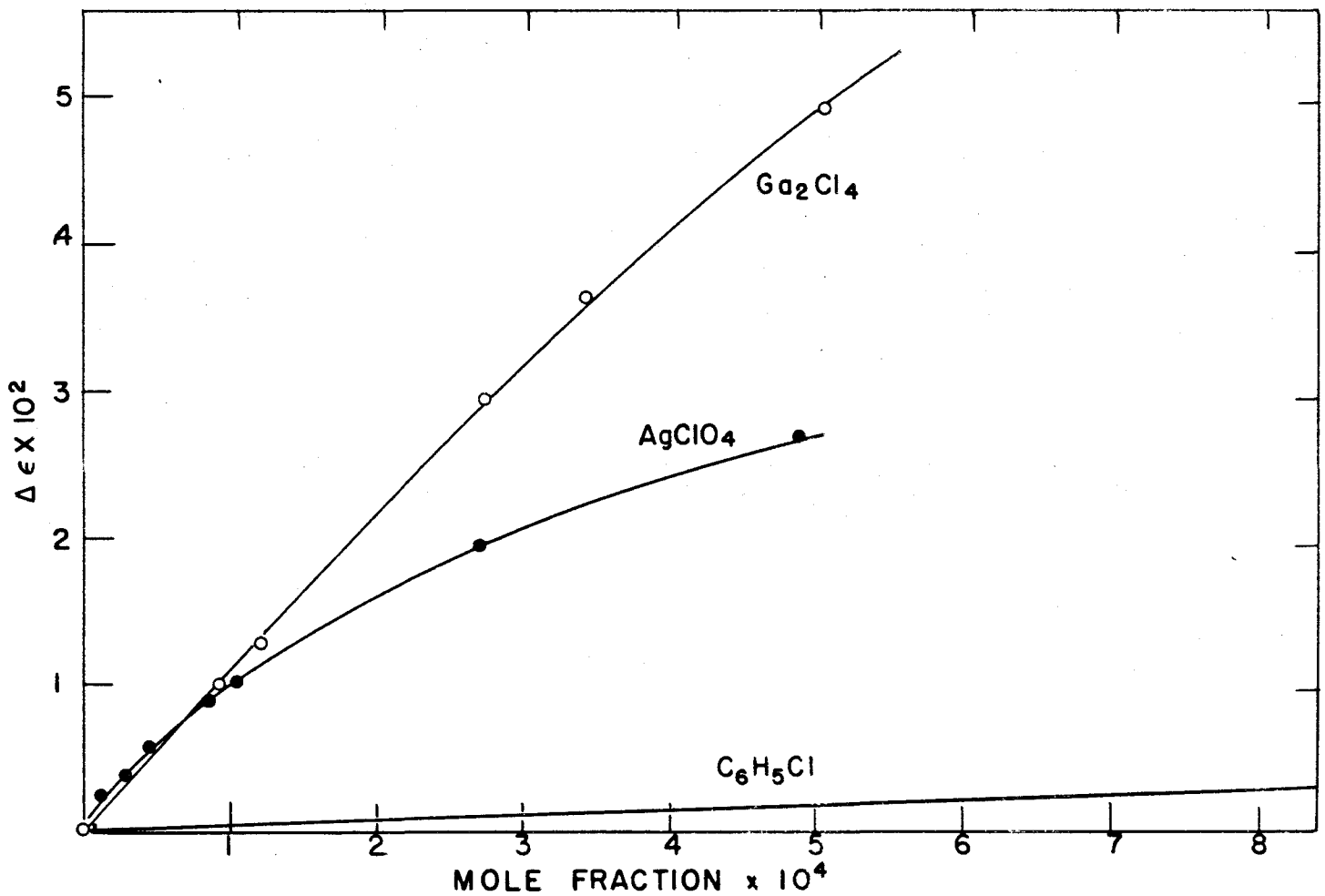
[a]Mole fractions based on formula weight of Ga_2Cl_4.

[b]Value taken from literature review by Trieber, Schurz and Koren (37).

[c]Concentration determined by spectrophotometric analysis.

[d]Concentration determined from weights of solvent and solute used.

Figure 9. Dielectric Constant of Benzene Solutions of Gallium Dichloride, Silver Perchlorate and Chlorobenzene


5
4
3
2
1
Δ ε X 10²
Ga₂Cl₄
AgClO₄
C₆H₅Cl
2
3
4
5
6
7
8
MOLE FRACTION x 10⁴

approximately one hundred times greater than that covered in the plot. This extrapolation appeared justified in view of the linearity found to exist in the concentration range investigated. The values for the chlorobenzene solutions were included in the figure so that the dielectric behavior of gallium dichloride solutions could be compared with that of solutions of a simple polar molecule. The silver perchlorate data were included to illustrate the dielectric behavior of benzene solutions containing a very polar inorganic molecule.

H. Solution Density Data

The experimental density data obtained at 25° for benzene solutions of gallium dichloride are given in Table 10. The absolute value for the density of pure benzene employed is that listed in the American Petroleum Institute Tables (39). It can be shown that a small error in the value taken for the density of benzene has little effect on subsequent dipole moment calculations, but rather, it is the rate of change of density with concentration that is important. The latter quantity can be accurately determined from the differential density values.

Table 10. Solution Density Data for Gallium Dichloride in Benzene at 25°

Mole fraction x 10^3 Ga_2Cl_4	Density g/ml
0.0000	0.87370[a]
0.6081	0.87475
1.065	0.87575
1.614	0.87695
2.099	0.87824
2.522	0.87902
3.698	0.88213
6.457	0.88872
8.640	0.89356

[a]Value taken from American Petroleum Institute Tables (39).

I. Estimated Dipole Moment of Gallium Dichloride

In order to calculate the dipole moment of gallium dichloride in benzene, the molar polarization of the solute at infinite dilution was determined by the method of Halverstadt and Kumler (40). From suitable plots of the experimental density and dielectric constant data listed in

Tables 10 and 9, the quantities

$$\lim_{X_2 \to 0} dv/dX_2 = \beta \qquad \text{and} \qquad \lim_{X_2 \to 0} d\epsilon/dX_2 = \alpha$$

were obtained, where v and ϵ are the specific volume and dielectric constant of the solution, and X_2 is the mole fraction of Ga_2Cl_4. The molar polarization of Ga_2Cl_4 at infinite dilution, $P_{2\infty}$, was calculated from the equation

$$P_{2\infty} = \frac{3\alpha v_1 M_1}{(\epsilon_1 + 2)^2} + (M_2 v_1 + M_1 \beta) \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \qquad (5)$$

where v_1, M_1 and ϵ_1 are, respectively, the specific volume, molecular weight and dielectric constant of the solvent, and M_2 is the molecular weight of the solute. The values of α, β and $P_{2\infty}$ were 106, -2.25 $cm.^3/g.$ and 1600 $cm.^3$, respectively. The dipole moment was calculated from the Debye equation

$$\mu = 1.28 \times 10^{-2} \left[(P_{2\infty} - P_d)T\right]^{\frac{1}{2}} \qquad (6)$$

where P_d is the deformation polarization of the solute and T is the absolute temperature. The value obtained is 8.9 Debye units, assuming that within experimental error P_d can be neglected in comparison with $P_{2\infty}$. If P_d is taken to be

approximately one-tenth the magnitude of $P_{2\infty}$, μ will be approximately five percent high.

I. Raman Data

The Raman investigation of benzene solutions of gallium dichloride yielded only one transition at $\nu = 341 \pm 5$ cm^{-1}. Within experimental error, a transition at the same frequency was observed for the benzene solutions of silver tetrachlorogallate. High background intensity may have obscured weaker lines.

V. DISCUSSION

A. Gallium(I) Halides

From the experimental results of this research, the following evidence can be presented for the existence of the gallium(I) halides. This evidence is drawn from two sources: (a) the phase diagram of the gallium-gallium triiodide system and (b) the measured solubility of gallium in gallium trichloride and in gallium tribromide.

From the results of the phase diagram study (Section IV, Parts C and D), it is apparent that gallium(I) iodide does exist as a stable compound both in the fused and solid states. The solid monoiodide has been isolated, and X-ray powder patterns have shown it to be distinct from gallium diiodide and gallium triiodide.

In the molten chloride and bromide systems, the magnitude of the metal solubility in the trihalides is evidence for the existence of less stable gallium monochloride and gallium monobromide. The mole ratios Ga/GaX_3, 0.529 and 0.654 respectively for the chloride and bromide (Table 3), represent the extent of reduction of the gallium trihalides by gallium. A ratio of 0.5 would correspond to reduction to only the dihalide, whereas a ratio of 2.0 would indicate complete reduction to the monohalide. Since the measured ratios are

significantly greater than 0.5, it is evident that appreciable amounts of gallium monohalide are formed in these reactions.

Disproportionation of the monochloride is observed on solidification of the melt, as indicated by the appearance of the grey color of finely-divided metallic gallium. This behavior is similar to that observed in other metal-metal halide systems in which the lower valent halide cannot exist as a stable solid phase (41). In the bromide system, however, gallium(I) bromide is stable as a solid phase.

The metal solubility data, therefore, indicate that the stability of the monohalides increases in the order chloride, bromide, iodide. A discussion of the disproportionation equilibria involving these compounds will be deferred to a later section since the reactions are related to the problem associated with the structural formulation of the gallium dihalides.

B. Structural Unit of Gallium Dichloride

The ionic unit $Ga(I)[Ga(III)Cl_4]$ is proposed as the basic unit of gallium dichloride. The experimental evidence which supports this formulation can be summarized as follows:

The cryoscopic evidence, graphically presented in Figure 8, clearly shows that the limiting value of the molecular weight of gallium dichloride in benzene at infinite dilution is 280 ± 5, as compared to the value 281.2 for the dimer Ga_2Cl_4.

The dielectric constant data (Figure 9) reveal that Ga_2Cl_4 in benzene is highly polar, the calculated dipole moment being 8.9 Debye units. These results are evidence that gallium dichloride exists in benzene as $Ga^+GaCl_4^-$ rather than the essentially nonpolar species $Cl_2Ga\text{-}GaCl_2$.

Comparative Raman studies of benzene solutions of Ga_2Cl_4 and $Ag(GaCl_4)$ reveal the same characteristic transition at 341 $cm.^{-1}$. This suggests that the tetrachlorogallate ion is common to both species. Further evidence that this assignment is correct is afforded by the observations of Taube and Wilson (42). They detected a single Raman transition at 337 cm^{-1} for solutions of gallium trichloride in concentrated hydrochloric acid. The one frequency observed in the three solutions can be assigned to the "breathing" vibration of the $GaCl_4^-$ anion, analogous to the assignment given by Woodward and Nord (43) for the most intense line of the Raman spectra of the $GaBr_4^-$ ion. The failure to detect the other three allowed transitions was probably due to the fact that the benzene solutions were quite dilute.

The preparation and properties of gallium(I) tetrachloroaluminate further substantiate the structure assigned to gallium dichloride. The compounds $Ga(GaCl_4)$ and $Ga(AlCl_4)$ can be considered as intermediates in the respective GaCl-$GaCl_3$ and GaCl-$AlCl_3$ systems. In contrast to the ambiguity of oxidation states in Ga_2Cl_4, the presence of the distinctive acid $AlCl_3$ in $Ga(AlCl_4)$ allows the identification of GaCl as the other component. That these two compounds are structural analogs is shown by the similarity of their physical and chemical properties. Gallium(I) tetrachloroaluminate melts at 175°, while gallium dichloride melts at 171°. As is shown in Table 8, the two compounds form aggregates in benzene, a behavior which will be discussed subsequently. On reaction with water, both compounds form a characteristic orange-brown precipitate from which hydrogen slowly evolves. This reaction can be attributed to hydrolysis of the unipositive gallium ion with attendant oxidation of the hydrolyzed species. During this reaction, a small amount of gallium is also produced, probably as a result of disproportionation which accompanies the initially vigorous solvolysis.

C. Solution in Benzene

Since it has been concluded that gallium dichloride exists as the ionic unit $Ga(I)[Ga(III)Cl_4]$, it is instructive

to consider qualitatively the dissolution of such ionic species as $Ga^+GaCl_4^-$, $Ag^+GaCl_4^-$ and $Ga^+AlCl_4^-$ in benzene. With these compounds, the solubility phenomenon appears to be a molecular dispersion of the $M^+MCl_4^-$ units without appreciable dissociation into ions; i.e., these units exist in solution as ion-pairs as do many ionic species in the vapor state. Of the numerous solutions of this type known, that of silver perchlorate in benzene has been the most extensively studied (44).

It is well known that a salt dissolves in a polar solvent with dissociation into ions only if the solvation energy is of the same order of magnitude as the lattice energy of the salt. Similarly, dissolution of a salt as a molecular dispersion is possible only if the solvation energy of the ion-pairs does not differ markedly from the heat of sublimation of the salt. The solubility in benzene of most ionic compounds, such as the alkali halides, is very small since the solute-solvent interaction is small compared to the heat of sublimation of the salt. However, with the compounds considered here, the low melting points would indicate small lattice energies and smaller heats of sublimation. Thus, the solvation energies necessary for dissolution of these compounds would not be as great as for the higher melting ionic compounds.

Evidence which suggests the nature of this solvation has been obtained from the extensive study of the complexes formed between the silver ion and unsaturated hydrocarbons (45, 46, 47). In these complexes, it is postulated that the π electrons of the hydrocarbons interact with the polarizing silver ion; this interaction has been described as an electron transfer bond by Mullikan (48). An acid-base interaction of this nature would thus account for the appreciable solubility of $Ag(GaCl_4)$, $Ga(GaCl_4)$ and $Ga(AlCl_4)$ in benzene. It is interesting to note that $Ga(GaCl_4)$ and $Ga(AlCl_4)$, like $AgClO_4$ (49), crystallize from benzene with solvent of crystallization.

As is seen from the cryoscopic data listed in Table 8, the apparent molecular weight of gallium dichloride and of gallium(I) tetrachloroaluminate depends strongly on concentration. This behavior has also been observed with silver perchlorate (50) and can be attributed to solute association resulting from strong coulombic interactions between the respective ion-pairs $Ga^+GaCl_4^-$, $Ga^+AlCl_4^-$ and $Ag^+ClO_4^-$. A comparison of the silver perchlorate and gallium dichloride data reveals that silver perchlorate is more extensively associated at comparable concentrations. The effect of association of gallium dichloride and of silver perchlorate is detected in the dielectric constant data shown in Figure

9, where the observed deviation from linearity reflects the reduced orientation polarization that accompanies the association of the solute into the multipolar aggregates. The fact that silver perchlorate is more extensively associated than gallium dichloride can account for the larger deviation observed in the dielectric data of silver perchlorate.

D. Treatment of Cryoscopic Data

An insight into the mode of aggregation of gallium dichloride in benzene can be obtained from an analysis of the cryoscopic data in terms of the equilibrium constants describing the association of Ga_2Cl_4 into the units $(Ga_2Cl_4)_2$, $(Ga_2Cl_4)_3$ ..... etc. For this analysis, it is assumed that Ga_2Cl_4 does not ionize to an appreciable extent in the concentration range studied, an assumption that has been substantiated for a large number of ion-pairs in benzene (51). Further it is assumed that the solvent behaves ideally, so that the cryoscopic measurement yields the true mole fraction of benzene from which the total number of distinct solute units can be inferred. Thus, solute-solute interactions other than those described by equilibrium constants are neglected.

If the association equilibria are written

$$2Ga_2Cl_4 = (Ga_2Cl_4)_2$$

$$3Ga_2Cl_4 = (Ga_2Cl_4)_3$$

$$\vdots$$

$$nGa_2Cl_4 = (Ga_2Cl_4)_n ,$$

the effective molality, m_e, and the stoichiometric molality, m_s, can be expressed as

$$m_e = \sum_{i=1}^{n} m_i = \sum_{i=1}^{n} K_i m_1^i \qquad (7)$$

$$m_s = \sum_{i=1}^{n} i m_i = \sum_{i=1}^{n} i K_i m_1^i , \qquad (8)$$

where m_i is the molality of $(Ga_2Cl_4)_i$, and the equilibrium constants, K_i, are defined by

$$K_i = \frac{m_i}{m_1^i} . \qquad (9)$$

Differentiating Equation 7 after m_1 and multiplying the derived equation by m_1 yields

$$m_1 \, (dm_e/dm_1) \; = \; \sum_{i=1}^{n} iK_i m_1^i \; = \; m_s \; . \qquad (10)$$

Hence,

$$\int_{\epsilon}^{m_e} dm_e/m_s \; = \; \int_{\delta}^{m_1} d \ln m_1 \; , \qquad (11)$$

where ϵ and δ are the values of m_e and m_1 at an arbitrarily low stoichiometric concentration. Since

$$\lim_{\substack{\epsilon \to 0 \\ \delta \to 0}} (m_1/m_e) \; = \; 1 \; ,$$

values of m_1 can be obtained from Equation 11 by fitting m_s as an analytical function of m_e and integrating. Hence, m_1 is obtained as a function of m_e. Equation 7 can be rewritten as

$$\frac{m_e - m_1}{m_1^2} \; = \; K_2 \; + \; \sum_{i=3}^{n} K_i \, m_1^{i-2} \qquad (12)$$

and the function on the left hand side of this equation evaluated from the values of m_1 calculated as above.

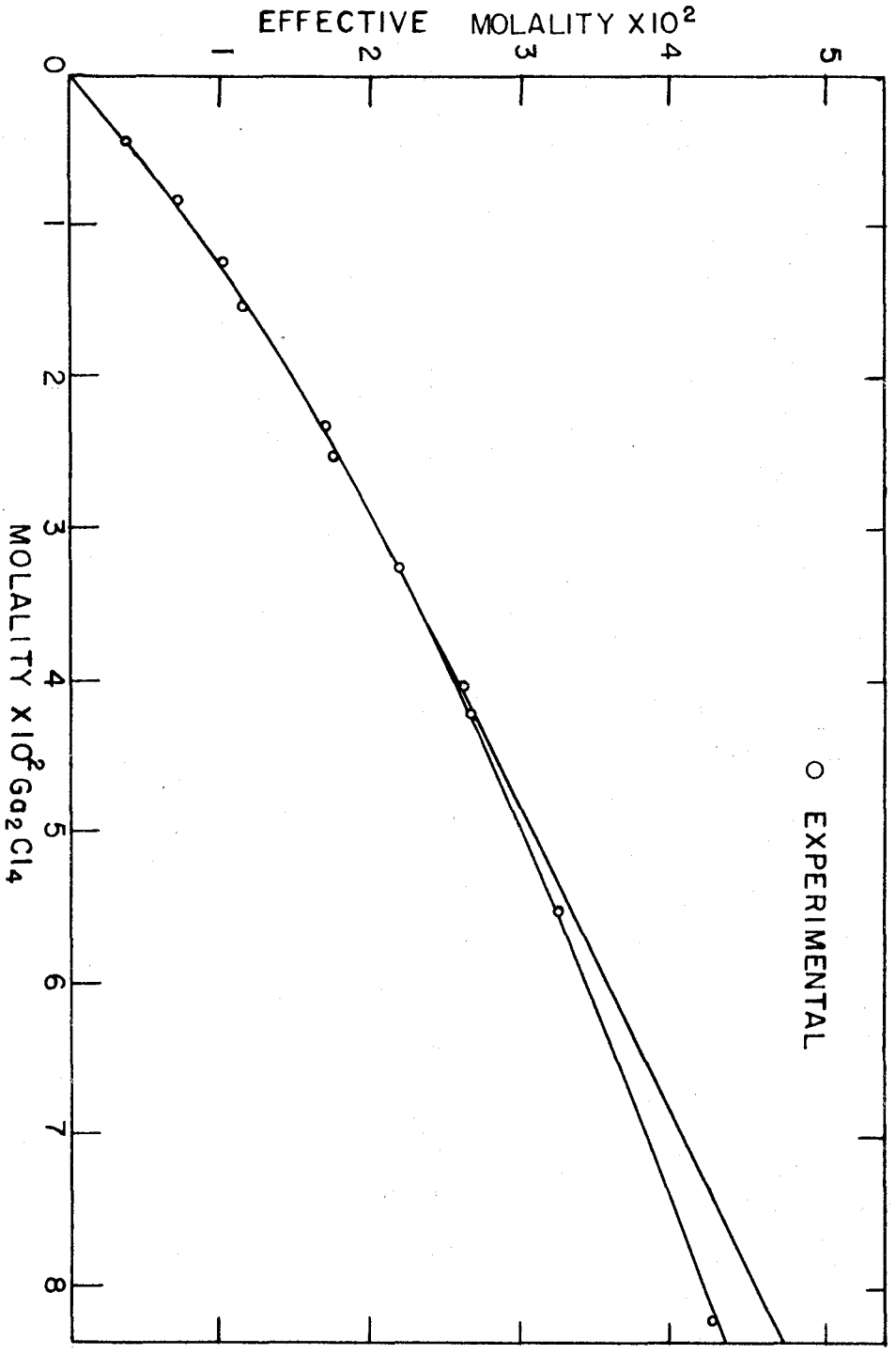
From a plot of the above function versus m_1, the equilibrium constants K_2 and K_3 were evaluated from the intercept and slope. A slight curvature of this plot indicated that K_4 and higher constants could be estimated, but it was felt

that the experimental accuracy did not justify their evaluation. Values determined for the first two constants were: K_2 = 10.8 molal^{-1} and K_3 = 1170 molal^{-2}.

As a test of the degree to which these two constants reproduced the data, m_e was calculated as a function of m_s and compared to the experimental m_e *vs.* m_s data, as shown in Figure 10. It can be seen that the curves are nearly coincident at low concentrations, while further association not described by the two equilibrium constants causes the experimental curve to lie below the calculated curve at higher concentrations. It should be pointed out that if this is due to association into $(Ga_2Cl_4)_4$, the concentration of this species at a given value of m_e would be one-fourth of the difference between the two curves.

From the constants K_2 and K_3, the free energies of formation of $(Ga_2Cl_4)_2$ and of $(Ga_2Cl_4)_3$ from Ga_2Cl_4 at infinite dilution were calculated using the hypothetical one-molal solution as the standard state. These values were: -1.32 kcal. for $(Ga_2Cl_4)_2$ and -3.42 kcal. for $(Ga_2Cl_4)_3$. Since it does not seem probable that linear association could account for the increased stability of $(Ga_2Cl_4)_3$, a different mode of association such as the formation of a cyclic unit may be indicated.

Figure 10. Experimental and Calculated Effective Molality of Gallium Dichloride as a Function of Stoichiometric Molality


EFFECTIVE MOLALITY X10²
0
1
2
3
4
5
MOLALITY X10² Ga₂Cl₄
1
2
3
4
5
6
7
8
O EXPERIMENTAL

The mole percentages of the three species Ga_2Cl_4, $(Ga_2Cl_4)_2$ and $(Ga_2Cl_4)_3$, calculated as functions of the stoichiometric molality of Ga_2Cl_4, are shown in Figure 11. The fact that a considerable fraction of the total mass of the solute is present as $(Ga_2Cl_4)_3$, even in the low concentration range, is graphic evidence of the stability of $(Ga_2Cl_4)_3$ with respect to $(Ga_2Cl_4)_2$. At the highest concentration shown on the graph, these three species account for 98.2 percent of the total weight of the solute.

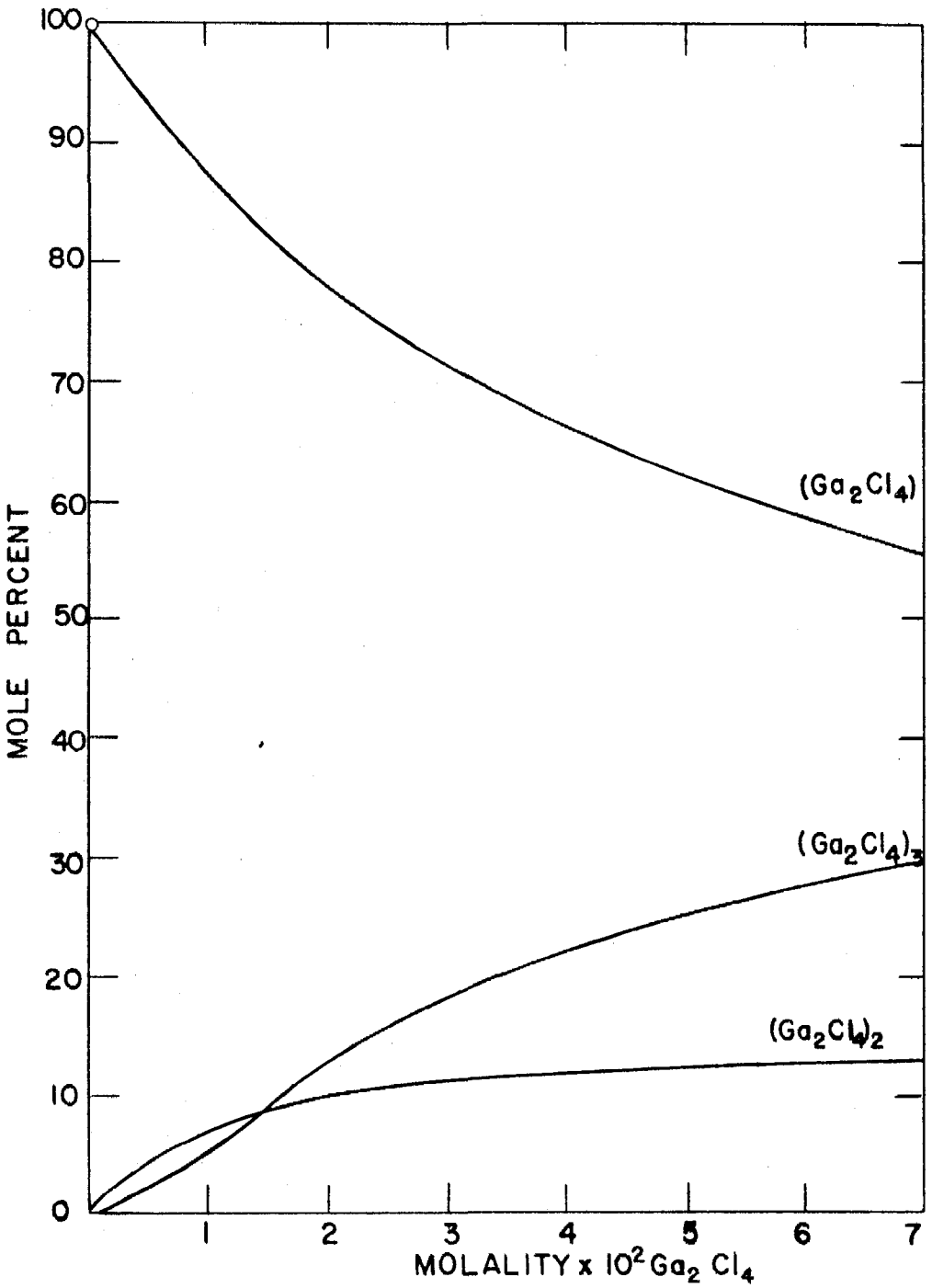
D. Disproportionation of Gallium Monohalides

It is proposed that the reaction

$$3Ga(I) = Ga(III) + 2Ga \qquad (13)$$

represents the disproportionation of the gallium(I) oxidation state since no evidence of dipositive gallium has been found. In the fused halide systems, the extent to which gallium(I) disproportionates should depend on the relative strengths of the gallium(I) and gallium(III) halide complexes formed in these basic systems. Since the complexes involving gallium(I) should be weak in comparison with those formed by the very acidic gallium(III), the above disproportionation equilibrium

Figure 11. The Calculated Distribution of the Species Ga_2Cl_4, $(Ga_2Cl_4)_2$ and $(Ga_2Cl_4)_3$ in Benzene


100
90
80
70
60
50
40
30
20
10
0
MOLE PERCENT
1
2
3
4
5
6
7
MOLALITY x 10² Ga₂ Cl₄
(Ga₂Cl₄)
(Ga₂Cl₄)₃
(Ga₂Cl₄)₂

can be qualitatively interpreted in terms of the stability of halide complexes of only the latter oxidation state. Further, since the equilibrium is established in the basic region of the GaX-GaX_3 systems, gallium(III) would be expected to exist primarily as GaX_4^-, the complex corresponding to the maximum coordination of gallium(III) with the chloride, bromide or iodide ion. (The basic region referred to is, therefore, that region containing halide ion in excess of the amount necessary for four-fold complexation.) Thus, for the fused halide systems, equation 13 should be written

$$3Ga^+ + 4X^- = GaX_4^- + 2Ga \qquad (14)$$

The relative extent to which the three monohalides disproportionate according to this reaction would be determined primarily by the effect that a change in halide ion would have on the stability of the GaX_4^- complex. The order of stability should be $GaCl_4^- > GaBr_4^- > GaI_4^-$, since gallium(III) shows greater affinity for the more electronegative halogens (52). In addition, halide-halide repulsion within the complex would also decrease the stability of the complex in the indicated order. Thus, the stability of unipositive gallium toward disproportionation should increase with increasing atomic weight of the halide. This interpretation is

consistent with the observed equilibrium concentrations of gallium(I) in the three systems. The mole percentages of gallium(I), as calculated from the metal solubility data presented in Table 3, are: for the iodide, 90.5; for the bromide, 59.3; and for the chloride, 51.9.

As expected, the relative stability of the monohalides in the solid state parallels that observed in the melt. The compounds GaBr and GaI are sufficiently stable to exist as pure phases, whereas GaCl disproportionates quantitatively according to the equation

$$4GaCl \longrightarrow Ga(GaCl_4) + 2Ga \qquad (15)$$

Thus, in forming the new phase, the disproportionation of GaCl proceeds only until sufficient $GaCl_3$ is produced to neutralize the basic chloride.

In contrast to the behavior described by equation 15, disproportionation of GaCl in the presence of an equimolar quantity of $AlCl_3$ is negligible both in the fused and solid states. As calculated from the metal solubility data listed in Table 3, the equilibrium concentration of gallium(I) in this fused system is 99.5 mole percent based on the total number of moles of gallium present. The solid phase which separates from the melt is $Ga(AlCl_4)$ rather than the $Ga(GaCl_4)$

formed in the absence of $AlCl_3$. It is possible, therefore, to stabilize unipositive gallium by the addition of a Lewis acid which shifts the equilibrium shown by equation 14 to the left by complexing the chloride ion. The function of $AlCl_3$ as a chloride acceptor in $Ga(AlCl_4)$ appears to be completely analogous to that of $GaCl_3$ in $Ga(GaCl_4)$.

In conclusion, it should be pointed out that the fused salt studies demonstrate a means whereby stabilization may be achieved for those subhalides of borderline stability. When the stability of the subhalide is limited by the acidic nature of the normal oxidation state, a condition which seems to be the case among the halides of the post-transition metals, the addition of an acidic molecule would be expected to enhance the stability of the lower oxidation state. That such is the case has been shown for the $Cd-CdCl_2$ and $Bi-BiCl_3$ systems, where 69 and 100 percent reduction to the unipositive state has been achieved in the presence of $AlCl_3$. Moreover, the subhalides formed are stable in the solid state (53). This is in contrast to the 17.6 and 46 percent reduction observed only in the melt under the more basic conditions present in the binary metal-metal halide systems (41). Beryllium, zinc, arsenic and antimony are other elements for which subhalide formation may occur upon solution of the metals in their respective subhalides (54). Studies of these

oxidation-reduction equilibria under acidic conditions may also prove that the isolation of the lower oxidation states is possible.

As pointed out in the Introduction, halides of the type M_2X_4 are known not only for gallium but also for the other elements of the group, indium and thallium. The formulation of the gallium dihalides as $Ga(I)[Ga(III)X_4]$ has presented the greatest problem in that not only were the gallium(I) halides unknown but there was also the alternate possibility involving metal-metal bonding. Since the problem has been resolved for the gallium compounds, there is now even more reason to believe that the indium and thallium salts are $M(I)[M(III)X_4]$ type compounds. In addition, gold may also form similar compounds, since $Au(AuCl_4)$ appears to be a likely product of the interaction of AuCl with the highly acidic $AuCl_3$.

E. Discussion of Errors

1. Cryoscopic measurements

Uncertainties in determining the effective molality by the use of a thermistor are discussed in the Appendix. More important errors were probably introduced in the preparation of the solutions. Approximately 100 g. of benzene was weighed

to within two milligrams; thus it is seen that no significant concentration error should have arisen from this measurement. An uncertainty of only 0.02 percent was introduced in weighing the solute since the total quantity of the material used was approximately one or two grams. In the apparatus used, benzene vapors did not come in contact with any soluble stopcock grease so that concentration errors due to dissolved contaminants were avoided. One indeterminate error in this experiment could have arisen from the hydrolysis of the solute or solution during the introduction of the sample. However, this error was minimized by the presence of argon over the solution and an atmosphere of helium in the ampule containing the salt. Nonetheless, that the principle errors were due to the hydrolysis is indicated by the fact that the average deviation in molecular weights determined in the standard naphthalene solutions (Appendix) was about 0.5 percent while the deviation in the molecular weights determined for hydrolyzable solutes was approximately twice as great.

2. Dielectric constant measurements

The temperature uncertainty of the solution in the Oscillometer was approximately 0.02°. Since the temperature coefficient of the dielectric constant of benzene is

1.1×10^{-3} deg.$^{-1}$ at 20° (37), the error thus introduced by this uncertainty was not detectable. The Oscillometer itself appeared to be capable of reproducing values of the change of dielectric constant, $\Delta\epsilon$, to within two percent. More significant errors of the experiment were thought to result from the uncertainty in the concentration determination. The maximum relative error in the mole fraction of the solute, as determined spectrophotometrically, was estimated to be about three percent. Therefore, the calculated value of the dielectric change with concentration, α, appeared to have a maximum error of five percent; however, the absolute accuracy of this value should be somewhat less.

3. Density measurements

It was believed that the greatest error introduced in the density measurements was caused by a temperature variation of approximately 0.2°. Since $\Delta d/\Delta t$ was found to be approximately 1.6×10^{-3} g. cm.$^{-3}$ deg.$^{-1}$ for these solutions, this would lead to an uncertainty in the density determination of about 0.03 percent. By comparison, errors in weighing with the fused silica microbalance would be insignificant. It can be shown that the constant β of equation 5, even if in error by five percent, would cause an error in the calculated dipole moment of less than 0.5 percent.

4. Preparation of materials

In order to assess the purity of the gallium dihalides, gallium(I) tetrachloroaluminate and silver tetrachlorogallate prepared by the methods described, the possible errors in the weights of the reactants should be considered. The relative weighing error for the volatile component was about 0.01 percent, while that for the metal was 0.03 percent. Hence, the maximum relative error due to weighing should be approximately 0.04 percent. Hydrolysis of the gallium and aluminum halides during the transfer operations could have been another source of error. Although the transfers were made *in vacuo*, water adsorbed on the walls of the containers could have caused a very small amount of reaction. This error was minimized by flaming the evacuated apparatus before the preparation.

VI. SUMMARY

The lower oxidation states in anhydrous gallium halides have been characterized by preparative methods and certain physical measurements.

The gallium dihalides (chloride, bromide and iodide) have been prepared by the reduction of gallium(III) halides with gallium or by the direct union of gallium and the halogens. Gallium(I) tetrachloroaluminate has been prepared by the reduction of gallium(III) chloride with aluminum or by the reduction of gallium(III) chloride with gallium in the presence of aluminum(III) chloride.

The phase diagram for the system gallium-gallium(III) iodide has been constructed. Gallium(III) chloride and gallium(III) bromide have been equilibrated with excess gallium (in the fused state) in order to determine whether gallium(I) chloride or bromide exists in a condensed phase.

X-Ray powder diffraction data have been obtained for the following compounds: gallium dichloride, gallium diiodide, gallium(III) iodide, gallium(I) iodide and gallium(I) tetrachloroaluminate.

The molecular weight of gallium dichloride has been determined cryoscopically in benzene using a thermistor as a resistance thermometer. Cryoscopic data have also been

obtained for gallium(I) tetrachloroaluminate. These measurements reveal that the basic unit of gallium dichloride is Ga_2Cl_4 and, further, that both gallium dichloride and gallium(I) tetrachloroaluminate form aggregates in benzene. The cryoscopic data for gallium dichloride have been analyzed in terms of association of Ga_2Cl_4 into $(Ga_2Cl_4)_2$ and $(Ga_2Cl_4)_3$.

The dielectric behavior of benzene solutions of gallium dichloride has been examined. Solution densities have been determined and the dipole moment of gallium dichloride calculated to be 8.9 Debye units.

The Raman spectra of gallium dichloride and of silver tetrachlorogallate have been obtained in benzene. The results indicate that the tetrachlorogallate anion is common to both solutes.

The following conclusions have been reached as to the nature of the lower oxidation states of gallium in the halide systems.

1. Gallium(I) iodide exists as a stable solid phase but melts with slight disproportionation into gallium diiodide and metal. In the fused state, gallium(I) chloride and gallium(I) bromide exist in equilibrium with gallium and the corresponding gallium dihalide, but only the monobromide is stable in the solid phase.

2. The basic structural unit of the gallium dihalides is $Ga(I)[Ga(III)X_4]$. The compounds are, therefore, intermediates in the GaX-GaX_3 systems.
3. In benzene, gallium dichloride exists as the highly polar ion-pair $Ga^+GaCl_4^-$ as do the species $Ag^+ClO_4^-$, $Ga^+AlCl_4^-$ and $Ag^+GaCl_4^-$. The aggregation observed with $Ga^+GaCl_4^-$ and with $Ga^+AlCl_4^-$ is due to the association of these dipolar species into multipolar units.
4. The extent of disproportionation of gallium(I) halides into metallic gallium and gallium(I) tetrahalogallates decreases in the order chloride, bromide, iodide because of the decreasing stability of the tetrahalogallate anion. It is possible to stabilize gallium(I) chloride by the presence of the Lewis acid $AlCl_3$ which complexes the chloride ion causing the disproportionation. The product, $Ga(AlCl_4)$ is structurally and chemically similar to gallium dichloride, $Ga(GaCl_4)$.

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IX. APPENDIX

Use of Thermistors in Cryoscopic Measurements

A summary of the method developed for the use of thermistors in cryoscopic measurements will be given here in order that the accuracy and applicability of the method can be evaluated by the reader. A more detailed description has been published in the literature (29).

Thermistors are semiconductors possessing large temperature coefficients of resistance. For this reason they have been applied in several instances to measurements of small temperature changes (28, 55, 56, 57). At room temperature, the temperature coefficient of resistance of the thermistor is twelve times that of the platinum resistance thermometer. Thus, an accuracy comparable to that possible with a platinum resistance thermometer can be obtained with a thermistor with considerably simpler apparatus. The resistance bridge, cryoscopic cell and techniques employed have been described in Section III. The purpose of this section is to develop the equation that relates the change in resistance of the thermistor at the freezing point of the solution to the effective molal concentration of the solute, and to show the applicability of this equation to the thermistor calibration.

It has been shown that over a temperature interval of several degrees, the resistance of a thermistor can be

expressed quite accurately as

$$\ln r/r_o = \frac{B\Delta T}{TT_o} , \qquad (1)$$

where B is a constant of the thermistor and T_o is any arbitrary reference temperature (58). For a dilute solution in which the solvent obeys Raoult's law, the thermodynamic expression for the variation of the freezing point depression, ΔT, with concentration is

$$-\ln X_1 = \frac{\Delta H^o \Delta T}{RTT_o} , \qquad (2)$$

where X_1, T_o and ΔH^o are, respectively, the mole fraction, freezing point and heat of fusion of the solvent. The equation

$$-\ln X_1 = \frac{\Delta H^o}{RB} \ln r/r_o \qquad (3)$$

is obtained by elimination of $\Delta T/TT_o$ from equations 1 and 2. If the usual approximation is made that

$$-\ln X_1 = \frac{m M_1}{1000}$$

where m is the molality and M_1 is the molecular weight of the solvent, and if $\ln r/r_o$ is expanded in terms of $\Delta r/r_o$,

where Δr is the resistance change corresponding to the freezing point depression, equation 3 can be written as

$$m = \frac{1000\,\Delta H^{o}}{RBM_1}\left[\Delta r/r_o - \tfrac{1}{2}(\Delta r/r_o)^2 + \cdots\right] \quad (4)$$

Equation 4 was used for the calculations of the effective molality from the resistance measurements.

The constant of the equation, $(1000\,\Delta H^{o})/RBM_1$, was experimentally determined from measurements of the change in thermistor resistance (corresponding to a lowering of the freezing point of the solvent) produced by the addition of phenanthrene in weighed increments to a known weight of benzene. For this calibration, it was assumed that the benzene obeyed Raoult's law over the concentration range investigated (zero to one mole percent solute).

The experimental data for the calibration of the thermistor are shown in Table 11. Experimental and calculated molality values are given for the corresponding resistance values. The deviations of the calculated from the experimental values of m tabulated in the last column give an indication of the accuracy of the method and the degree to which equation 4 fits the data. The average deviation is 2.2×10^{-4} molality units; this is about one-half to one-

Table 11. Calibration Data for the Thermistor in Benzene

r_o ohms	Δr ohms	$m \times 10^2$	$m \times 10^2$ calc.	$\Delta m \times 10^4$
2299.10	0.00	0.000	0.000	---
	6.29	1.313	1.266	4.7
	12.42	2.502	2.496	0.6
	18.14	3.624	3.642	-1.8
	22.76	4.567	4.565	0.2
	28.08	5.640	5.626	1.4
	34.92	6.996	6.983	1.3
	49.53	9.921	9.875	4.6
2288.93	0.00	0.000	0.000	---
	7.52	1.530	1.520	1.0
	14.88	2.983	3.003	-2.0
	25.23	5.038	5.079	-4.1
	32.87	6.581	6.608	-2.7
	43.13	8.649	8.647	0.2
	52.82	10.609	10.570	3.9
			Av. dev.	2.2

fourth of that reported in the literature for other similar measurements with thermistors (55, 56).

The source of the apparently systematic trend in the deviation shown in Table 11 is not known. The trend in the deviations suggest that additional small terms are needed for a description of the thermistor resistance by equation 1. Non-ideality of the system can, of course, be responsible for the observed deviations at the higher concentrations although it does not seem probable that the trend could be attributed solely to this factor over the entire concentration range. The approximation of X_1 in terms of m and the omission of ΔC_p in the derivation of equation 4 have been found to increase the deviation by only 15 percent without affecting the character of the trend (29).

As a test of the accuracy with which molecular weights could be determined, the system naphthalene in benzene was studied. From measurements on ten concentrations of naphthalene up to 0.101 molal, an average molecular weight of 128.08 $\pm$ 0.66 was calculated, as compared to 128.18 for the theoretical value. The direct comparison of the results obtained simultaneously with a Beckman thermometer showed the greater accuracy of the thermistor method. The molecular weights calculated from differential thermometer readings had twice as large an average deviation with a nearly random

scatter about the correct value. Remarkably accurate values of the heat of fusion of benzene were obtained when values of B determined from the comparative Beckmann readings were applied to the constant $(1000\ \Delta H^{o})/BRM_{1}$ obtained in the thermistor calibration (29).

One difficulty encountered here was the tendency of the thermistor to undergo slow changes in resistance over a period of time. However, for the type of work described herein, this factor has been substantially eliminated by the use of the expression relating the concentration and the ratio of the resistance change to the resistance at the freezing point of pure benzene. This required only that r_{o} did not change during the run, a condition which was found to hold. The two series of measurements shown in Table 11 were purposely chosen to determine the extent to which a small change in r_{o} affected the calibration. The runs were carried out seven weeks apart, during which time, as a result of various treatments, r_{o} had changed by several tenths of a percent. Moreover, the first set of data was obtained with undried benzene at one atmosphere (not the usual procedure), while the second was obtained under the vapor pressure of the solution using dry, vacuum-distilled benzene. The effect of pressure on the freezing point of benzene has been reported as 0.003^{o} deg. $atm.^{-1}$ (59). While this would

affect the value of r_o only slightly, an unknown but apparently small concentration of water condensed from the air would give an added increase to r_o. Much smaller differences between values of r_o were found when the data were obtained under similar conditions only a few days apart.